PB84-102565

Estimation of the Importance of Condensed Particulate Matter to Ambient Particulate Levels

PEDCo-Environmental, Inc., Durham, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Apr 83

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. NA	2.	3. RECIPIENT'S ACCESSION NO. PB84 102565
4. TITLE AND SUBTITLE Estimation Of The Importance Of Condensed Particulate Matter To Ambient Particulate Levels		5. REPORT DATE April 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Pedco Environmental, Inc.		8. PERFORMING ORGANIZATION REPORT NO. PN 3525-37
9. PERFORMING ORGANIZATION NAME AND ADDRESS Pedco Environmental, Inc. 505 S. Duke St. Durham, NC 27701		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency Office Of Air Quality Planning And Standards Research Triangle, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

EPA Project Officer: Harold G. Richter

16. ABSTRACT

This study attempts to quantify, by means of published and unpublished data, the fractions of particulate emissions from major sources which is condensed matter unaccounted by emissions inventories. Very few reliable quantitative data were found. Most of the estimates in the report are based on front half/back half data from EPA Method 5 tests. The contractor estimates that 30 - 50 percent of point source particulate emissions in certain cities could be condensed matter. However, the reliability of these estimates is questionable because of an artifact problem. Thus, estimated emissions may be too high for some sources and too low for others.

An appendix summarizes the data found.

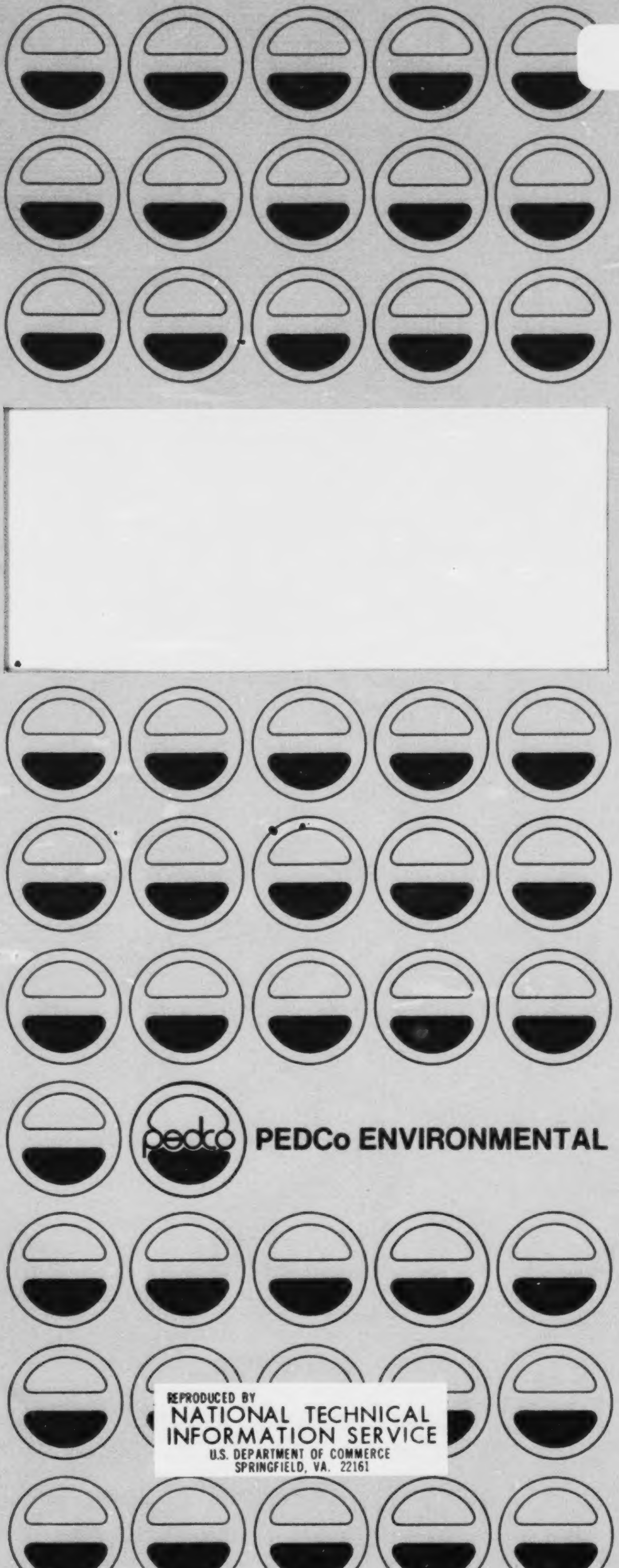
17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 133
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-102565



PEDCo ENVIRONMENTAL

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ESTIMATION OF THE IMPORTANCE OF CONDENSED PARTICULATE MATTER TO AMBIENT PARTICULATE LEVELS

Prepared by

PEDCo Environmental, Inc.
505 South Duke Street, Suite 503
Durham, North Carolina 27701-3196

Contract No. 68-02-3512
Task Order No. 37
PN 3525-37

Task Manager

Harold G. Richter, Ph.D

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

April 1983

This report has been reviewed by the Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, and approved for publication as received from Pedco Environmental, Inc. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, neither does mention of trade names or commercial products constitute endorsement or recommendation for use.

CONTENTS

	Page
Figures	v
Tables	vi
Acknowledgment	vii
Executive Summary	viii
1. INTRODUCTION	1
1.1 Purpose of this study	1
1.2 Approach	2
2. CHARACTERIZATION OF CONDENSED PARTICULATE MATTER	3
2.1 Definition of condensed particulate matter	3
2.2 Properties that characterize condensed particulate matter	4
2.3 Reference points for condensed particulate data comparison	4
3. CONDENSED PARTICULATE MATTER FROM STATIONARY SOURCES	7
3.1 Estimation of condensed particulate matter by source category	7
3.2 Estimation of condensed particulate matter as primary sulfate emissions	18
3.3 Test methods for stationary sources	19
3.4 Control of condensed particulate matter from stationary sources	22
4. CONDENSED PARTICULATE MATTER FROM MOBILE SOURCES	27
4.1 Light-duty vehicles	27
4.2 Heavy-duty vehicles	28
4.3 Test methods for mobile sources	29
4.4 Mobile source impact in an urban situation	29
4.5 Future mobile source trends	30
5. CASE STUDIES OF POTENTIAL CONDENSED PARTICULATE MATTER EMISSIONS IN THREE CITIES	32
5.1 Houston, Texas	32
5.2 Philadelphia, Pennsylvania	36
5.3 Portland, Oregon	36

CONTENTS (continued)

Page

6. EFFECT OF CONDENSED PARTICULATE ON AMBIENT PM_{10} 41

- 6.1 Primary and secondary particulates studies 41
- 6.2 Visibility impairment 44
- 6.3 Impact based on National emissions data reports 47
- 6.4 Recommendations for future study 47

REFERENCES 51

GLOSSARY 55

Appendix A Formation of condensed particulate matter A-1
Appendix B Filterable vs. condensed particulate matter and adjusted emission factors B-1
Appendix C Discussions of EPA Methods 5 and 17, modifed Method 5, and the stack dilution sampling system C-1
Appendix D Control techniques for condensed particulates D-1
Appendix E Test methods for mobile sources including data summary and correction factor E-1

FIGURES

Number		Page
1	Average Number, Surface Area, and Volume Distributions of Los Angeles Smog	5
2	Summary of Relative Source Contributions for Sites	20
3	Eight-day Average of Daytime Fine- and Coarse-fraction Mass Concentrations Apportioned by Chemical Species in Houston from September 11 to 19, 1980	46
4	Contributions to the Mean Daytime Light Extinction Coefficient in Detroit	47

TABLES

Number		Page
1	Potential Stationary Sources of Condensed Particulate	8
2	EPA Method 5 Test Results--Ratio of Front Half (Filterable) to Back Half Particulates by Source Type	10
3	Estimated Percents of Ambient Sulfate Levels Due to PSE for Different Geographical Regions of the U.S.	21
4	Examples of Process Modifications to Reduce Condensed Particulate	24
5	Estimated Total Cost of Reducing Condensed Particulate Emissions (September 1982 dollars)	26
6	1973 Stationary Source Particulate Matter, Estimated Condensed Particulate, and Estimated Total Particulate Emissions from Source Types in the Houston-Galveston Urban Area that Generate Greater than 100 tons/year (tons/year)	33
7	Stationary Source Particulate Matter, Estimated Condensed Particulate, and Estimated Total Particulate Emissions in the Houston-Galveston Urban Area Based on TACB Permit Applications after 1973 (tons/year)	35
8	Total Stationary Source and Estimated Condensed Particulate Emissions in Philadelphia Neighborhood Scale Study (tons/year)	37
9	Estimated Total Particulate Emission Rates in Portland Airshed	39
10	Relative Contribution of Condensed Particulate Matter to Fine Particulate in Portland	40
11	Major Selected Source Categories of Condensed Particulate	48
12	Stationary Source Categories Accounting for Two Percent or More of 1978 Actual Particulate Emissions	49

ACKNOWLEDGMENT

This report was prepared for the U.S. Environmental Protection Agency by PEDCo Environmental, Inc., Cincinnati, Ohio. Dr. Harold G. Richter was the EPA Project Officer. Mr. William G. DeWees served as the Project Director, and Mr. Vinson Hellwig was the Project Manager. The principal authors at PEDCo were Mr. Vinson Hellwig, Mr. Joseph Steigerwald, and Mrs. Barbara Allen. Sections of this report were authored by Dr. Joseph Sickles, Research Triangle Institute, and Dr. Guy Oldaker, Entropy Environmentalists, Inc. The authors thank Dr. Richter for his overall guidance, direction, and comments on this study. The authors also thank the California Air Resources Board, Pennsylvania Department of Environmental Resources, and the South Coast Air Quality Management District for making available unpublished data for this study.

EXECUTIVE SUMMARY

Condensed particulate matter[a] results from chemical reactions as well as physical phenomena. The findings of this report indicate that whereas inorganic species form condensed particulate matter by physical condensation, chemical reactions, agglomeration, and nucleation, organic species from stationary and mobile sources form condensed particulate matter primarily by physical condensation. Almost all condensed particulate matter is formed in the <10 micron range, referred to as PM_{10}.

PEDCo gathered test data for 60 stationary source categories to determine the ratio of condensed particulate (assumed to be represented by the back half of the Method 5 sampling train) to filterable particulate (represented by the front half of the EPA Methods 5 and 17 sampling trains). Due to limited data, this relationship was the best available means of estimating the significance of condensed particulate matter for a large number of stationary sources. This technique, however, overestimates some source categories while underestimating others. Therefore, the data estimates are suitable for program guidance only and should not be considered as actual contributions.

Based on this relationship, PEDCo then conducted several analyses to evaluate the existing data base on particulate emissions from several stationary source categories. The following summarize the results of this evaluation.

- A review of the 10 major stationary source contributors of particulate emissions determined by a 1978 OAQPS study indicated that the current estimated particulate emissions would have to be increased by 27 percent to account for condensed particulate,[1] if only these source categories were considered.
- A review of the 10 major stationary source contributors of particulate emissions in a 1978 DSSE study (67.3% of total emissions) indicated that the current estimate of particulate emissions would have to be increased by 30 percent to account for condensed particulate.

---

[a] A definition of condensed particulate is presented in Section 2.1 of this report.

- Condensed particulate accounted for 30 percent, 48 percent, and 22 percent of the total primary stationary source particulate emissions in the Houston, Texas; Philadelphia, Pennsylvania; and Portland, Oregon areas, respectively. All of these studies were smaller in size than their respective Air Quality Control Region (AQCR).

The above impacts account only for the contribution from stationary sources; the percentages do not represent the total impact on PM_{10}. The total impact on ambient air would be significantly less on a percentage basis since background sources contribute little condensed particulate matter and some categories such as mobile sources account for condensed particulate matter in emissions inventories.

A review of studies conducted in Houston and Detroit indicated that fine particulate can impair visibility by creating a highly visible plume. Since condensed particulate forms mostly fine particulate, it should have a similar effect. Although the total impact could not be estimated using the available data, sufficient evidence exists to indicate the need for further investigation of this problem.

Methods available for control of condensed particulates from stationary sources fall into three categories: 1) process or raw materials modifications that remove or reduce the amounts of the species present, 2) process modifications that would cause a shift in the size of particles in the effluent to particles greater than 10 μm in diameter, and 3) collection of the condensed particulate with control devices. Although some modifications to process and raw materials are feasible for reducing condensed particulate, in some cases, this might only delay the eventual formation of PM_{10} through secondary particulate formation. Control technology exists for many sources of condensed particulate; however, the cost per pound of particulate collected is generally much greater for condensed particulate than for filterable particulate.

This study also included an assessment of the test methods currently being developed for use on stationary sources to measure condensed particulate. A state-of-the-art condensed particulate matter sampling system has been developed by EPA's Industrial Environmental Research Laboratory (IERL), but thus far it has had limited field use. The principles of dilution and sample collection by IERL's Stack Dilution Sampling System (SDSS) have been confirmed in part by a similar sampling system used on mobile sources by the Environmental Sciences Research Laboratory (ESRL). The mobile source sampling system has had extensive evaluation and field use.

Sciences Research Laboratory (ESRL). The mobile source sampling system has had extensive evaluation and field use.

This study also evaluated the results of various ambient sampling studies to determine the impact of condensed particulates on ambient air quality. An analysis of these sampling studies indicates that in more heavily industrialized urban areas, up to half of the PM_{10} is primary sulfate, secondary sulfate, and nitrate.[3] It also can be inferred that up to one-fourth of the area's particulate matter could have been condensed particulate based on the contribution from sulfates and mobile sources. This was based on the findings that the ambient particulate attributed to both sulfates[4] and mobile sources[19-21] are up to one-half condensed particulate.

The data base that was developed and researched for this report did not provide an adequate foundation to establish the exact contribution of condensed particulate matter to PM_{10}. Unfortunately, most total suspended particulate (TSP) or PM_{10} studies do not relate the stationary source contributions directly to the ambient monitoring results. This analysis indicates a need for further study to address current test methods for measuring particulate matter emissions and to resolve the question regarding primary and secondary particulate formation at the receptor site.

It should be noted that a significant portion of the findings in this report are based only on estimates. The results, however, indicate clearly that further studies should be undertaken to provide accurate data acquisition techniques and to conduct ambient studies to determine whether State and local agencies must consider condensed particulate in the development of their control strategies for attaining current or revised TSP Nation Ambient Air Quality Standards (NAAQS). As additional data are acquired, the resulting data bases and emission factors should be updated accordingly.

SECTION 1

INTRODUCTION

Section 109(d) of the Clean Air Act as amended in 1977 requires the U.S. Environmental Protection Agency (EPA) to review the air quality criteria for the total suspended particulate (TSP) National Ambient Air Quality Standards (NAAQS) by December 31, 1980, and at 5-year intervals thereafter. As a result of these reviews, the EPA may revise the air quality criteria and promulgate new NAAQS in accordance with Sections 108 and 109(b) of the Clean Air Act.

Since the promulgation of the TSP NAAQS in 1971, the need for promulgation of a NAAQS for size-specific particulate matter has been of considerable concern to EPA.[5] Because of this concern, EPA has committed a substantial research effort toward studying the sources, effects, and transport of those particulate matter size fractions believed to have the greatest impact on health and welfare.

The EPA is now in the process of reviewing the current TSP NAAQS with regard to the requirements in the Clean Air Act as amended in 1977. As part of this review, the Agency has collected, analyzed, and evaluated a wide variety of data on health and welfare effects and on emissions and ambient air quality. Some of these data provide information on condensed particulate matter.

1.1 PURPOSE OF THIS STUDY

Because of the manner by which particulate matter is measured in stack gases, the mass of the condensed particulate matter is generally not included in calculations of particulate matter emission factors. Moreover, if the condensed particulate matter is a significant fraction of TSP and particulate matter with an aerodynamic particle size diameter of 10 µm or less (PM_{10}), strategies to reduce ambient levels of TSP or PM_{10} may be less effective than estimated initially. If the States are to develop effective control strategies for PM_{10}, EPA must ascertain the importance of condensed particulate matter to ambient levels of PM_{10}. The objectives of this study were 1) to obtain engineering and emission data on potential stationary sources of condensed particulate matter and 2) to estimate the impact of condensed particulate matter on ambient TSP and PM_{10} air quality and on visibility. In addition, if condensed particulate matter was determined to be a major contributor to ambient air quality, control techniques and emission testing methods were then reviewed and discussed. Wherever possible, potential modifications to existing data bases and emission factors are also discussed.

The ultimate goal of the study is to estimate the impact of condensed particulate matter on ambient TSP and PM_{10} levels and to identify those stationary sources that may be the major contributors of condensed particulate matter in the United States.

1.2 APPROACH

Although no source tests were performed or special ambient studies conducted as part of this effort, a number of source test reports were reviewed and the data were evaluated to determine the potential impact of condensed particulate. Data from ambient studies dealing with condensed particulate matter and unpublished source test data from the files of the EPA Emissions Measurement Branch and the States of California, Pennsylvania, and North Carolina, were also reviewed and evaluated in an effort to summarize the available information on condensed particulate matter.

A literature search was conducted to establish a comprehensive list of studies dealing with condensed particulate matter. These studies were then reviewed, and pertinent data were extracted and analyzed. Because the data on condensed particulate matter are limited, much of this report is based on extrapolated data and/or good engineering judgment.

In addition to summarizing all available data on condensed particulate matter, PEDCo selected three urban areas for case studies to estimate the potential impact of condensed particulate matter emissions on ambient air quality: Houston, Texas; Philadelphia, Pennsylvania; and Portland, Oregon. Relative PM_{10} contributions from several source categories were estimated on the basis of available data for these areas, and adjustments were made to particulate matter emission inventories to account for estimated condensed particulate.

SECTION 2

CHARACTERIZATION OF CONDENSED PARTICULATE MATTER

The term "condensed particulate matter" has been used in various contexts without a widely accepted definition. Since the main goal of this study is to determine the significant stationary source contributors of condensed particulate matter, the definition pertains only to stationary source emissions and excludes all filterable particulate matter collected by EPA Method 5.

2.1 DEFINITION OF CONDENSED PARTICULATE MATTER

Condensed particulate matter is defined in this report as material that is a gas or a vapor at the stack temperature at the sampling location which transforms into a liquid or solid from immediately after the sample location to within a few seconds after it leaves the stack or duct. The two major requirements for formation of condensed particulate matter are 1) the stack effluent is diluted with the ambient air approximately tenfold, and 2) the mixed stack effluent quickly comes to ambient temperature. In most cases both of these requirements will be met within a few seconds and a few hundred feet after exiting the process or stack. The condensed particulate matter can form both in or out of the stack as a result of cooling. When the filtration temperature (usually $250^{o}F$) of the EPA Method 5 is less than the stack temperature, a portion of the filterable particulate may be condensed particulate matter. However, this portion of condensed particulate matter is not included in this report since it is currently regulated as particulate and is included in the emissions inventory.

In contrast, secondary particulate is a product of atmospheric chemical reactions and requires several minutes, hours, or days to form. Because the definitions allow some slight overlap between what is considered to be condensed particulate matter and what is considered to be secondary particulate, a refined definition of particulate must describe temperature, pressure, and other factors of collection techniques. Therefore, particulate collected by reference method condensed particulate matter train must exactly define "condensed particulate matter" in terms of the previously mentioned parameters.

2.2 PROPERTIES THAT CHARACTERIZE CONDENSED PARTICULATE MATTER

Chemical and physical mechanisms influence aerosol formation and growth. Chemical reactions produce a compound that may convert from gas to form a particulate, and such reactions may occur in or on the particle. To a large extent, nucleation, condensation, absorption, adsorption, coagulation, and sedimentation determine the size distribution of aerosols.

Particulate matter exists in various sizes, both at the source and in the atmosphere. Size distributions of aerosols can be based on number, surface area, and volume (or mass). Figure 1 shows the number, surface area, size, and volume distributions of Los Angeles smog.[6,7]

In ambient air, the volume (or mass) distribution is usually bimodal, with a demarcation between fine and coarse particles occurring between 2 and 3 μm particle diameter. Coarse particulate matter typically originates from natural and anthropogenic mechanical processes and comprises approximately two-thirds of the aerosol mass. Fine particles typically originate from combustion sources and the condensation of chemical or photochemical reaction products.

Fine particles may show two surface area modes.[6,7] The first mode (at approximately 0.02 μm) results from direct emissions of combustion products. The second (between 0.1 and 0.5 μm) results from the coagulation of primary particles or the condensation of reaction products or water on primary particles. The latter is known as the "accumulation mode," because aerosols that grow into this range by coagulation and condensation tend to remain in this range.

By number, most of the particles are smaller than 0.1 μm. Particles of this size are produced by nucleation in combustion sources and by gas-to-particle conversion processes such as occur in urban atmospheres; this is known as the "nucleation" mode. A more detailed discussion of particle formation is presented in Appendix A.

2.3 REFERENCE POINTS FOR CONDENSED PARTICULATE DATA COMPARISON

Strategies for the control of particulate matter from stationary sources currently focus on emissions of primary particulate matter and their relationship to measured ambient particulate matter levels. Ideally, the cause-and-effect relationship between emitted particulate and particulate matter

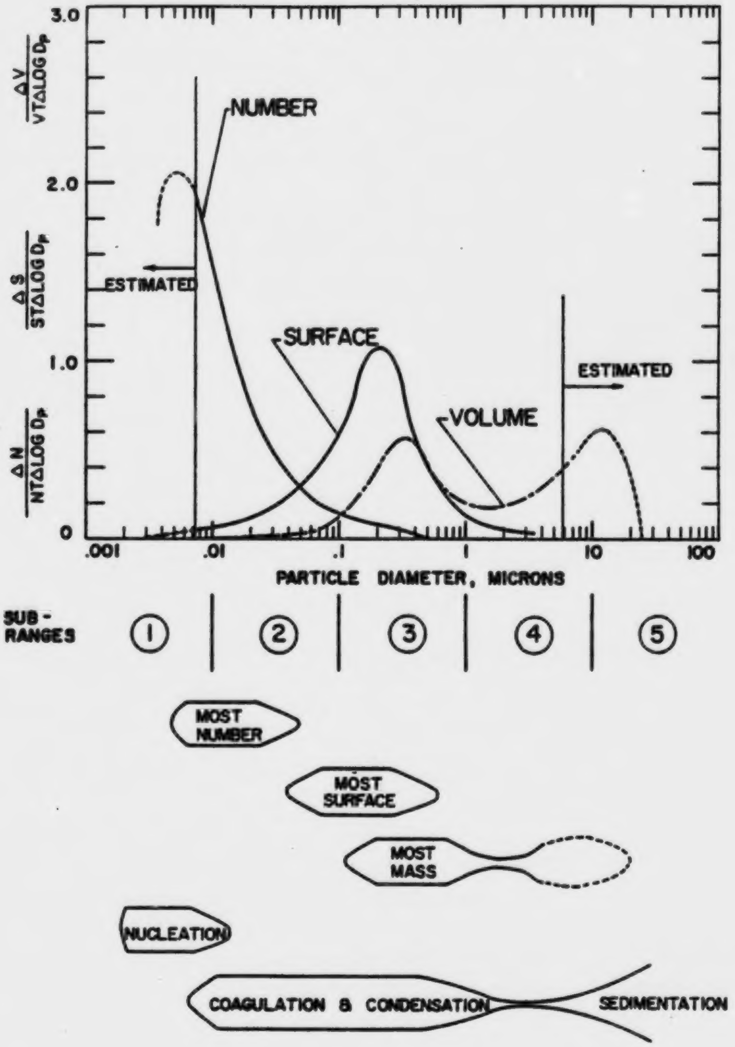


Figure 1. Average number, surface area, and volume distributions of Los Angeles smog.[a]

---

[a] The linear ordinate, normalized by total number, area, or volume, is used so that the apparent area under the curves is proportional to the quantity in that size range. The principal mechanism affecting the growth and removal of particles in each size range is also given.[7]

measured at ambient conditions could be established by simply determining particulate matter emissions from the stationary sources. Although data are available on particulate matter emissions for many stationary source categories, these data cannot necessarily be used in a straightforward way to estimate the total particulate matter emissions. According to 40 CFR 60, the current definition of particulate matter is any solid or liquid matter collected by the EPA Reference Methods 5 and 17, but this definition applies only to filterable particulate. Actual emissions from sources would consist of both filterable and condensed particulate matter. The total impact on the ambient particulate level from any source would be some portion of the primary (filterable and condensed) and the secondary particulate matter that is formed later as a result of atmospheric reactions. The impact is a function of both the particle size distribution of the primary particulate and the conversion rate and ratio of the secondary particulate formation.

SECTION 3

CONDENSED PARTICULATE MATTER FROM STATIONARY SOURCES

A variety of stationary sources emit gaseous vapors that condense in the ambient air to become particulate matter. Condensed particulate emissions form from both organic and inorganic compounds and are generated by fossil fuel combustion, incineration, and various industrial processes. Table 1 presents a list of potentially significant stationary sources of condensed particulate.

3.1 ESTIMATION OF CONDENSED PARTICULATE MATTER BY SOURCE CATEGORY

EPA Method 5 source test data from the Emission Measurement Branch (EMB) of the EPA and the States of California, Pennsylvania, and North Carolina were reviewed to estimate the condensed particulate levels from stationary sources. The "front half" (or filterable portion) of each test and the "back half" (or impinger catch) were tabulated to determine their contribution to the total sample. For the purpose of this analysis, the condensed particulate was assumed to be the particulate present in the impinger catch.

By use of Method 5 data from various sources and the tabulation of data as "back-half" versus "filterable," the relative contribution of condensed particulate from source categories was estimated. The data bases were limited, however, and no allowance was made for artifact formation in the impingers or particle size distribution of the collected sample.

Table 2 summarizes the EPA Method 5 results used in this study. It presents the ratio of filterable particulates and back-half catch to total particulate collected in Method 5 tests of 60 process source categories. These data represent one or more source tests.

All data collected are shown in Appendix B. Appendix B also contains a table presenting emissions estimates based on adjusted AP-42 emission factors for selected process source categories. The AP-42 emission factors were adjusted to account for increased particulate wherever the appropriate source categories could be matched with the data in Table 2. This increase would be

TABLE 1. POTENTIAL STATIONARY SOURCES OF CONDENSED PARTICULATE

- Alfafa dryers
- Anode baking furnaces
- Asphalt plants
- Asphalt roofing
  - Felt saturating
  - Asphalt blowing
- Boilers/other combustion
  - Bagasse
  - Coal
  - Lignite
  - Oil
  - Wood/bark
- Charcoal kilns
- Chemical production
  - Boric acid
  - Phosphoric acid
  - Potassium still
  - Zinc sulfate
- Citrus peel dryers
- Coke plants
- Corn processing
  - Wet milling
  - Syrup manufacturing
- Elemental phosphorus
- Electric arc furnace
- Expanded vinyl
- Ferroalloy mills
- Fertilizer plants
  - Ammonium nitrate
  - Diammonium phosphate
- Fiberboard
  - Dryer
  - Press
- Fiberglass and mineral wood
  - Curing ovens
  - Blow chambers
- Glass plants
- Grain dryers
- Gray iron foundries
- Incinerators
- Iron and steel mills
  - Sinter plant
  - Electric arc furnace
  - Basic oxygen furnace
  - Open hearth furnace
  - Sand blasting
  - Heat treating
  - Scrap steel melting
- Kraft pulp and paper mills
  - Recovery boilers
  - Lime kiln
  - Smelt dissolve tank
  - Blow tank/hot water accumulator
- Lime kiln
- Manure dryers
- Mineral products
  - Gypsum
  - Clay dryers
  - Feldspar dryers
  - Clay kilns

(continued)

TABLE 1 (continued)

Petroleum refineries
- FCC
- Catalytic regenerator
- Heaters
- Petroleum coke

Portland cement plants
- Kiln
- Finish mill

Primary nonferrous smelters
- Al Soderberg furnace
- Cu converter
- Cu electric furnace
- Cu fluid fed roaster
- Pb sinter line
- Pb blast furnace
- Mo roasters
- Zn ore briquet dryer
- Zn sweat kiln
- Zn fume kiln

Residential heating
- Oil
- Wood

Rubber curing press

Rubber incineration

Secondary metal smelters
- Al scrap furnace
- Al dross furnace
- Brass and bronze furnaces
- Cu furnace
- Pb furnaces
- PbO_2 mills
- Pb grid coating
- Pb remelt pot
- Other metal furnaces

Sewage sludge incinerators

Silicon carbide furnaces

Spray paint booths

Sulfite pulp mill
- Recovery boiler
- MME blow tanks

Textile
- Nylon polymerization
- Melt polymer spinning
- Tenter frame
- Dye beck
- Heat set
- Texturizing
- Latex backing

Tire buffing operations

Wood products
- Veneer plant dryer
- Resawing

TABLE 2. EPA METHOD 5 TEST RESULTS--RATIO OF FRONT HALF (FILTERABLE) TO BACK HALF PARTICULATES BY SOURCE TYPE[a]

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Anode baking furnace	65.8	34.2	7
Asphalt plants	67.9	32.1	17
Boiler/coal (industrial)	90.1	9.9	10
(utility)	55.6	44.4	15
Boiler/oil	42.7	57.3	27
Boiler/wood	84.0	16.0	14
Brick and tile kilns	72.2	27.8	9
Chemical production			
Potassium still	65.3	34.7	1
Chrome oxide kiln	94.3	5.7	1
Boric acid	44.1	55.9	2
Electric arc furnaces			
BOF	62.9	37.1	3
Open hearth	77.3	22.7	3
Coke ovens	71.7	28.3	4
Sandblast	68.2	31.8	2
Heat treating	69.9	30.1	2
Elemental phosphorous	46.0	54.0	1
Fiberboard dryer	57.5	42.5	2
Glass plant	73.0	27.0	14
Grain dryers	74.5	25.5	3
Incinerators			
Municipal	69.7	30.3	4
Industrial	35.3	64.7	1
Sewage sludge	61.8	38.2	2
Iron and steel			
Iron foundries	76.4	23.6	6
Iron and steel sinter plants	70.8	29.2	14
Kraft pulp			
Recovery boilers	85.7	14.3	10
Lime kiln	60.9	39.1	6
Smelt dissolve tank	83.8	16.2	6
Lime kiln	89.6	10.4	3

(continued)

TABLE 2 (continued)

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Mineral products			
Gypsum	87.3	12.7	1
Clay dryer	0.5	99.5	1
Feldspar dryer	11.6	88.4	1
Clay kiln	87.4	12.6	2
Mineral wool	60.7	39.3	3
Petroleum refineries			
Heaters	45.6	54.4	1
FCC	76.1	23.9	2
Catalytic regenerator	46.6	53.4	3
Portland cement			
Kiln (gas-fired)	90.1	9.9	1
(coal-fired)	73.8	26.2	1
(wet-process)	65.5	34.5	8
(dry-process)	37.9	62.1	1
(process not specified)	46.4	53.5	1
	81.1	18.9	1
	82.9	17.1	1
	48.0	52.0	1
Finish mill (wet-process)	73.6	26.4	3
Primary nonferrous smelters			
Zinc sweat kiln	24.7	75.3	1
Zinc fume kiln	86.6	13.4	1
Zinc ore briquet dryer	82.7	17.3	1
Lead sinter line	95.6	4.4	2
Lead blast furnace	37.7	62.3	1
Copper converter	69.5	30.5	1
Copper converter, electric arc furnace, and fluid bed roaster	39.8	60.2	1
Copper reverberatory furnace	44.5	55.5	1
Copper roasters	99.0	1.0	1
Molybdenum roasters	97.0	2.9	1
Roofing			
Saturated felt	55.7	44.3	2
Asphalt blowing	56.8	43.2	4

(continued)

TABLE 2 (continued)

Source type	Particulates, %		Number of test reports
	Filterable	Back half	
Secondary metal smelters			
Aluminum dross furnace	11.1	88.9	1
Aluminum furnace	33.7	66.3	1
Lead furnace	44.2	55.8	7
Lead mill	47.2	52.8	1
Lead grid casting	52.3	47.7	4
Lead remelt pot	89.8	10.2	1
Nonferrous metal reclamation furnace	64.5	35.5	3
Silicon carbide furnaces (Acheson furnace)	68.3	31.7	4
Spray paint booths	62.2	37.8	4
Textile			
Dryers	24.7	75.3	1
Tenter frame	14.1	85.9	4
Wood products			
Sanding	73.4	26.6	3
Resawing	91.7	8.3	2

[a] Test results reflect emissions after air pollution control equipment.

generally will not correlate with the percentage condensed particulate shown in Table 2. The adjusted AP-42 emission factors were calculated based on the determination of the condensed particulate rate from specific tests that most closely fit the description in AP-42. The determination was made using the units shown in AP-42 (e.g., lb/ton).

It should be noted that the condensed particulate emission rate will be the same whether the source is uncontrolled or controlled to any degree since the condensed particulates form after the control equipment. Therefore, on a mass rate basis this quantity generally does not change with the application of typical control equipment. The percent condensable particulate data in Table 2 and the adjusted AP-42 emission factors should correlate only when the control efficiency is the same for both. The adjusted AP-42 emission factors were not used for any studies in this report.

The adjusted emission factors would be more indicative of the true total particulate impact on the TSP ambient air quality levels. For the emission factors for a size-specific particulate matter standard, the filterable particulate portion would need to be reduced to include only the regulated particle size range of each test. The adjustment for particle size distribution was beyond the scope of this task.

In addition to the data available from the Method 5 tests, information on condensed particulate was also available for the following source categories as discussed below:

- Kraft pulp and paper
- Portland cement plants
- Primary nonferrous smelters
- Textile industry.

3.1.1 Kraft Pulp and Paper

Investigations of out-of-stack aerosol formation as a result of emissions from kraft pulp mills have indicated that these emissions are significant sources of cloud condensation nuclei (CCN).[8,9] One study indicated that a large portion of these emissions is less than 1 μm.[9] The assumption was made that these particles might be the products of SO_2-NH_3-H_2O (liquid) reactions. Also, a portion of the CCN was attributed to sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), and sodium sulfite (Na_2SO_3), all of which were believed to have condensed in the ambient air.

liquors. The recycling of bleach liquors appears to be the major source of chlorine. The amount of chlorine in black liquor has increased significantly since mills are recycling effluent streams and normal outlets have been reduced; i.e., the equilibrium in the system has shifted.

Also, the increased use of low-odor recovery boilers has resulted in an increase in the weight of sodium sulfate lost from the boilers. In low-odor boilers, total reduced sulfur is reduced by shifting the chemical equilibrium to form sodium sulfate instead of SO_2. As a result of this shift, a higher amount of Na_2SO_4 is emitted. Because of the higher flue gas temperature (~218°C), a portion of the material is in the vapor phase when it exits the electrostatic precipitator (ESP). Because of the increased amount of sodium sulfate and sodium chloride in the fume, the particle size is reduced.[11]

3.1.2 Portland Cement Plants

The portland cement industry is a good example of a potential condensed particulate emitter that was studied to determine the cause of these emissions. One such study was prompted by a problem resulting from the formation of a bluish-white detached plume at a portland cement plant stack in Glens Falls, New York. This plume, which occurred intermittently and only during humid and cool weather conditions, did not appear to be a typical water vapor plume. Under an EPA grant, the University of Denver performed an extensive investigation of the Glens Falls cement kiln to evaluate the condensed particulate formation in the plume.[12] The Glens Falls plant, which is a dry process plant (raw material crushing and mixing), uses an ESP for particulate control. The ESP was originally designed for a wet process plant; however, rather than replacing it, the plant installed a water injection system downstream of the kiln and upstream of the ESP to condition and cool the exhaust gases to the ESP.

The results of the study showed that the plume contained various species of sulfates: ammonium sulfate, ammonium bisulfate, and sulfuric acid. Stack tests (12 runs) performed on the facility showed that the stack gases contained an average of 171 ppm of ammonia and 204 ppm of sulfur oxides (in the gaseous state) and 20 percent moisture content.[13]

After laboratory research and analysis of the condensed plume, the following mechanism for formation of the ammonium sulfate compounds was proposed:

the SO_2 dissolves in the condensed water vapor along with NH_3; the NH_3 shifts the pH of the system and forces the reaction $SO_2 + H_2O \rightarrow HSO_3^- + H^+$; further shifts in the pH forces the reaction $HSO_3^- \rightarrow SO_3^= + H^+$. Because the pH has shifted and the SO_2 has converted to HSO_3^- and $SO_3^=$, it is more easily oxidized than SO_2. The predominant resulting reaction is:

$$3NH_3 + 2SO_2 + 3H_2O + \tfrac{1}{2}O_2 \rightarrow (NH_4)_2SO_4 + NH_4HSO_4 .$$

Because some sulfuric acid is also present in the system, the condensed particulate consists of ammonium sulfate, ammonium bisulfate, and some sulfuric acid.[12]

Raw materials that are used in the manufacture of portland cement contain varying amounts of volatile alkali compounds. When exposed to the intense heat of the calcining kiln, this material volatilizes and combines with water, SO_2, and chlorides in the gas stream. The species formed include NaOH, Na_2SO_4, NaCl, KOH, KCl, K_2SO_4, and $SO_3^=$. Relative amounts of each species vary depending on feed rate, relative amounts of feed alkali, temperature, and kiln conditions. As these species exit the kiln, they either condense as fine particles and penetrate farther into the last fields of the ESP and are emitted or condense on larger particles in the gas stream. Selective removal of large particles (CaO, $CaCO_3$, SiO_2) in the inlet fields results in a particle size shift to fine alkali compounds in the exit gas stream. The method of condensation (as fine particles or as coating on large particles) is determined by the relative concentration of particles in the hot gas stream, the predominant chemical species, and the rate of cooling.

This detached plume phenomenon has been observed at several other portland cement plants, therefore, this problem, is not unique.

3.1.3 Primary Nonferrous Smelters

Sources of condensed particulate emissions from pyrometallurgical smelting include lead sintering operations, copper roasters, and furnaces. Both copper and lead smelting have two processes that emit condensed particulate. Some of this particulate is in the form of sulfuric acid and sulfates formed from the SO_2 in the lead sinter line off-gases and copper roasters, but most of it is emitted in the form of a metallic oxide fume from the furnaces (i.e., arsenic trioxide).

Arsenic emission rates from copper smelters equipped with pollution controls range from 0.1 to 36.5 kg/h (0.3 to 80.4 lb/h) in the United States. Much of the arsenic leaves the control equipment in a vapor state and condenses in the ambient air, unless gas cooling is performed before the control device.[14]

3.1.4 Textile Industry

Organic materials are used in all processing steps in the textile industry. Oils are applied during spinning, throwing, and knitting to reduce friction and minimize yarn damage; detergents are used as scouring aids; the dyeing process and the dyes themselves include the use of softeners, antifoaming agents, and dye accelerants or carriers; and finishing may include treatment with water-repellent, flame-retardant, soil-resistant, antistatic, and crease-resistant materials. Drying and heat treatment of fabrics play an important role in textile processing, and the relationship between the retained and/or process-vehicle organic material on the fabric or yarn and the drying of heat-treatment conditions largely defines the potential for condensed organic emissions.[15]

Three studies were conducted on various textile finishing operations in plants in North Carolina.[16,17,18] One study determined the manner and amount of organic carrier emitted to the atmosphere during the dyeing of polyester fabric in dye becks open to the atmosphere. The data indicate that the carrier, biphenyl, was emitted at a rate equal to 42 to 50 percent of the initial charge during the dye cycle. The dye beck is maintained at 100°C (212°F) after the charge and during the dyeing process and the boiling point of biphenyl is 256.1°C (493.0°F).[16]

A modified EPA Method 5 sampling train was used to test the emissions. The biphenyl was collected in the impingers and analyzed by gas chromatography. The tested emission rate was 586 kg/Mg (1,171 lb/ton) of charged biphenyl for the dye beck. All of the biphenyl collected was in the back half of the sampling train and was considered condensed particulate.

The second study was a source test (similar to the first one for biphenyl) performed on a loop dryer at a different plant in North Carolina.[17] The loop dryer was used to dry cloth after the dyeing process was complete. Two tests were conducted with a modified EPA Method 5 sampling train. The biphenyl was collected in the back half of the train and analyzed by gas chromatography. The resulting biphenyl emissions were 8.4 kg/Mg (16.8 lb/ton) of cloth or for the two drying lines, 33.7 kg/h (74.3 lb/h) of biphenyl (condensable organic compound).

The third study was an analysis of ambient pollutant particulate data collected near two textile finishing plants.[18] The organic particulate matter was extracted from ambient filters with benzene, and the benzene extract was analyzed by gas chromatography.

Gas chromatographic analyses of suspected organic compounds and stearic and palmitic acids (used in the process at one plant) were compared with the extracted organic material from the ambient filters. The resulting chromatographic retention times on the same column and at the same conditions were identical. The organic fraction on this filter exceeded 78 $\mu g/m^3$.

A similar analysis for suspected organic compounds (stearic, palmitic, and oleic acids) used in the process at the second plant was compared with the extracted organic material from the ambient filters. The resulting retention times on the same column and at the same conditions were identical. The organic fraction of this sample was 146 $\mu g/m^3$.

No attempt was made in this study to determine the ratio of condensed particulate matter to noncondensed organic emissions, nor was a measurement made of the efficiency of the collection of these compounds on the filter media.

Additional data indicate that the curing of latex backing on drapery and upholstery fabrics results in the loss of substantial amounts of organic fractions. The emission is primarily composed of stearic acid, oleic acid, and palmitic acid. The rate of emission and the visible opacity are related to usage rates in the chemical formulation and curing temperature. Reported rates were 2 to 3.6 kg/1000 kg of fabric processed.

With the exception of a minor amount of fiber lost (~0.45 kg/h), all of the particulate emissions from textile processing is in the form of a hydrocarbon aerosol. The condensation temperature for most processes is between 49°C (120°F) and 121°C (250°F).

3.2 ESTIMATION OF CONDENSED PARTICULATE MATTER AS PRIMARY SULFATE EMISSIONS

Sulfates account for a significant portion of the TSP in urban areas. Because a major fraction of urban atmospheric sulfate is contained in particles smaller than 2 μm in diameter, sulfates are a major constituent in the ambient PM_{10}. Based on the data available, it appears that primary sulfate emissions (PSE) from coal and oil combustion may account for 50 percent or more of ambient sulfate levels in certain Air Quality Control Regions (AQCR's).[4]

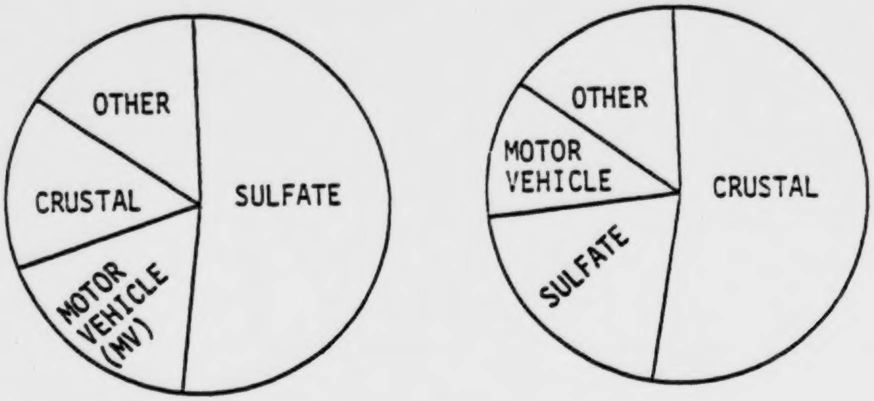
Uncontrolled combustion of residual oil in utility boilers results in a mean conversion of 4.45 percent of the fuel sulfur to primary sulfates. Of this primary sulfate, approximately 36 percent is particulate sulfate; the remainder is comprised of gaseous sulfur trioxide, sulfuric acid, and sulfuric acid mist. Uncontrolled combustion of pulverized bituminous coal in utility boilers results in a mean conversion of only 1.41 percent of the fuel sulfur to primary sulfates. The sulfate is distributed approximately equally between particulate and gaseous/mist phases. The EPA reference method collects the particulate sulfate and some of the acid mist and may convert and collect some of the gaseous sulfur compounds. Although all of the acid mist and gaseous pollutants generally would be considered as condensed particulate matter, the condensed particulate matter portion that is collected with the filterable particulate is regarded as filterable particulate for this study and in the emission inventories.

Despite the significance of both primary and secondary sulfates, neither is specifically regulated on either a source or ambient basis, with a few minor exceptions. The relative contributions of primary and secondary sulfates will vary from region to region, depending upon emission patterns and the amount of $SO_4^=$ formed in, transported into, and removed from the regional ambient air. Man-made contributions to ambient sulfates are composed of three sources: (1) regional primary sulfate emissions, (2) regional secondary sulfate formation, and (3) extra-regional contributions attributed to long-range transport and transformation of sulfur oxides. Anthropogenic primary sulfate emissions can be characterized as arising from combustion, transportation, or areawide sources. The relative contribution of each source type can vary substantially in different localities. The rate of regional formation of sulfates by local atmospheric conversion of SO_2 is dependent upon atmospheric conditions in the region. High humidity and the presence of catalysts such as nitrates, olefins, sulfates and chlorides of iron and manganese, and ammonia can increase the conversion rate of SO_2 to sulfate by several orders of magnitude from the rate in clean air. The importance of regional secondary sulfate formation hinges not only on the rate of conversion of SO_2 to sulfate, but on the amount of time locally-generated SO_2 resides in the regional air environment before it is transported into other regions. Ambient sulfates resulting from long-range transport of primary and secondary sulfates can comprise an important fraction of total ambient sulfates in regions which are not meteorologically isolated from other regions. Combustion source emissions, rather than area or transportation source emissions, would be expected to be transported far from the source because they are emitted at greater heights above the ground.[4]

A cursory examination of the factors noted above can be made to give estimates of the percent of total ambient sulfates which are primary sulfates in certain regions of the U.S. For example, in eastern cities (e.g., New York), the ratio of PSE to total sulfur emissions is high due in great part to oil-fired combustion sources. But while the amount of regional secondary sulfate formation is probably average, the extraregional contributions of sulfate (both primary and secondary) are quite high. Here the percentage of ambient sulfates due to PSE is probably about 50 percent. In nonurban areas of the East, emission densities are less, but extraregional contributions to the ambient sulfate level from both primary and secondary sulfates are still high. In these cases, PSE probably contributes only 20 to 50 percent of the total ambient sulfates. Isolation of a region can prevent extraregional contributions of sulfate. So in isolated regions, local PSE generally comprise a larger proportion of ambient sulfate levels. Table 3 summarizes regional data on the contributions of PSE to total ambient sulfate.[4] Figure 2 gives the contribution of sulfate compared to the other major contributors of a typical urban and nonurban ambient particulate concentration. These are given for both coarse and fine particulate.[3]

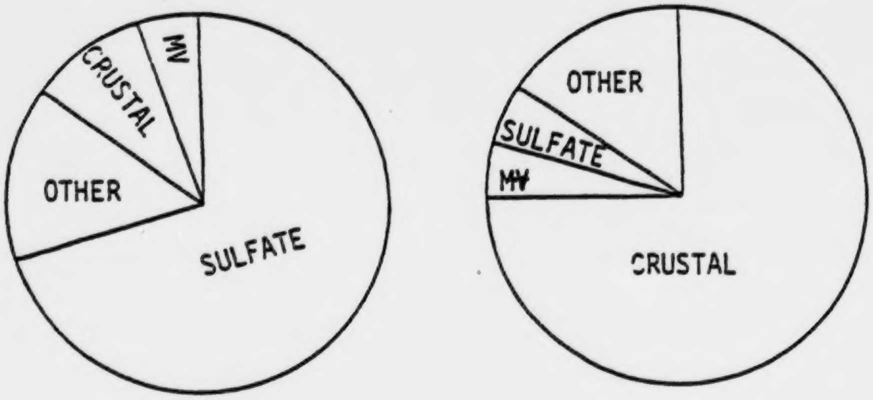
3.3 TEST METHODS FOR STATIONARY SOURCES

Although several methods are currently available for measuring particulate matter mass concentrations within stationary source effluent streams, not all of these methods will produce results that are representative of primary



≤2.5 µm 2.5 - 30 µm

URBAN



≤2.5 µm 2.5 - 30 µm

NONURBAN

Figure 2. Summary of relative source contributions for sites.

TABLE 3. ESTIMATED PERCENTS OF AMBIENT SULFATE LEVELS DUE TO PSE[a] FOR DIFFERENT GEOGRAPHICAL REGIONS OF THE U.S.[3]

Region	Percent of ambient $SO_4^=$ due to PSE
East and midwest east of Mississippi River, urban	Up to 50%
West, urban; also other isolated urban sites	50% or more
Los Angeles Basin	20 to 50% (only 10 to 40% of ambient $SO_4^=$ due to regional coal and oil combustion in stationary sources)
East and midwest, nonurban	20 to 40%
West, nonurban	Not meaningful due to very low emissions and transport factors

[a] As used here, PSE include primary sulfates from all regional and extra-regional sources, not merely regional coal and oil combustion. The true percentage will depend on local PSE patterns and the relative contribution of combustion, area, and transportation sources.

particulate matter emissions. Some methods are intended for quantifying levels of filterable particulate matter, whereas others can produce results that more accurately approximate the contributions of both filterable and condensed particulate matter.

The most widely used test methods for particulate emissions from stationary sources are EPA Methods 5 and 17. Both methods rely on a filter media to trap the particulate matter for measurement. Appendix C contains discussions of Methods 5 and 17, a modified Method 5 (including impinger catch), and a stack dilution sampling system (SDSS) to provide a general understanding of how the test results from each are related to the formation of condensed particulate matter in the effluent stream.

Technically valid interpretations of data on particulate matter mass concentrations require an understanding of the method used to obtain the data. This requirement is particularly important with regard to the problem of predicting primary particulate matter emission factors from available data. Thus, the available data base can be used effectively for the purpose of this study if the user understands how well the data obtained from the sampling methods account for the condensed particulate portion of the effluent sample.

Based upon the current level of understanding that has been briefly summarized, a general hierarchy can be formulated that shows how the results of commonly available methods and the levels of primary and filterable particulate matter relate to each other. Accordingly, when the condensed particulate phenomenon exists, the mass concentrations of particulate matter may be expected to take the following order:

Filterable particulate matter = **Particulate matter determined by Reference Method 17** ≤ **Particulate matter determined by Reference Method 5** < **Particulate matter determined by Stack Dilution Sampling**[a] = **Primary particulate matter** ≤ **Particulate matter determined by modified Reference Method 5**[a]

3.4 CONTROL OF CONDENSED PARTICULATE MATTER FROM STATIONARY SOURCES

Methods available for control of condensed particulates from stationary sources fall into three main categories: 1) modifications to processes and raw materials to remove or reduce the amounts of the species present, 2) process modifications that result in a particle size shift in the effluent to larger fractions, and 3) collection of the condensed particulate matter in add-on control devices. The formation of secondary plumes outside the source stack represents a separate and complex control methodology and is discussed separately.

3.4.1 Process Modifications

Most condensed particulate matter results from the introduction of a raw material or contaminant into a high-temperature industrial process. The volatilization of the species results in the selective loss of the material in the effluent stream as a gas and the condensation of a compound as the gas stream temperature is reduced. The point of condensation may be within the ductwork, stack, or outside the stack, depending on the chemical species and/or the gas stream temperature. The condensed material may be solid or liquid, depending on chemical composition and temperature. Removal or reduction of the volatile components in the process feed is an effective method of reducing condensed aerosol emissions. Examples of processes in which this technique has been applied are asphalt concrete plants, expanded vinyl curing, fiberboard dryers, fiberglass and mineral wool curing ovens, electric arc furnaces, kraft pulp recovery boilers and lime kilns, expanded aggregate kilns, municipal incinerators, portland cement finish mills and kilns, secondary metal furnaces (aluminum, brass, copper, lead), and textile operations (melt polymer spinning, heat setting, texturing latex backing curing). Table 4 lists source emissions and specific process changes that have been used to reduce aerosol formation.

---

[a] See Appendix C for discussion of SDSS and modified Method 5.

Process modifications also may include the use of chemicals that change volatile components to a less volatile form. The use of oil treatments, which poison the vanadium in residual oils and reduce its action in the formation of SO_3 aerosol, is an example of this method. These applications also include chemical reactions that cause an element to be removed as a result of high volatility. Selective injection of $CaCl_2$ to a portland cement kiln shifts the equilibrium to form KCl instead of KOH or K_2SO_4. The volatility of KCl allows the species to be withdrawn through the alkali bypass system and collected. This reduces the loss of KOH and K_2SO_4 from the tower ESP. Chemical treatment is used less frequently and must be applied on a case-by-case basis, depending on process chemistry and product requirements.

Process modifications also may be made that allow the condensation of particles to occur on the surface of larger particles in the gas stream. The control of gas stream temperature, concentration of particles, and rate of cooling is necessary to prevent the condensation of the condensed particulate matter. Interferences such as particle polarity and gas stream moisture also have an influence on particle partitioning. It appears that since the number of particles in the gas stream is reduced as a result of higher collection efficiencies (fabric filters and ESP's), heavy metals condense as separate aerosols. These aerosols form high-opacity plumes of low mass (i.e., very small particles), which have become evident in coal- and oil-fired boilers, cement kilns, and primary smelter operations.

Gas streams that contain volatile species may pass through conventional control devices before the particulate matter can condense to a solid or liquid droplet. A process control modification that allows the gas stream to be cooled before entering the control device has been proven to be an effective control option. Serious technical problems arise in the process if the gas stream contains high concentrations of water vapor or corrosive gases (SO_3, HCl, HF), or when the condensed particulate matter is composed of hydrocarbon

TABLE 4. EXAMPLES OF PROCESS MODIFICATIONS TO REDUCE CONDENSED PARTICULATE

Source category	Aerosol	Process change
Asphalt plant (drum mix)	Hydrocarbon (oils)	Move asphalt injection point; use lower volatility asphalt; reduce aggregate temperature.
Expanded vinyl	Hydrocarbon (plasticizer)	Change plasticizer formulation; improve low volatility component; reduce curing temperature.
Fiberboard dryers	Hydrocarbon (wax, resin)	Use higher melting paint wax; change thermoplastic resin; reduce dryer temperature; eliminate hot spots in gas stream.
Fiberglass curing ovens	Hydrocarbon (resin)	Change resin formula; reduce curing temperature.
Mineral wool blow chamber	Hydrocarbon (oils)	Change point of injection of annealing oil; use less volatile annealing oil; reduce usage rate.
Electric arc furnace (secondary steel)	Hydrocarbon (oil)	Reduce percentage of oil in turnings; segregate poor quality scrap (zinc, paint); use optimum charge technique; improve burning above charge.
Kraft pulp (recovery boiler)	Condensed fume (NaCl, SO_3)	Reduce Cl content of black liquor; reduce excess air.
Kraft pulp (lime kiln)	Condensed fume (Na_2O)	Improve lime mud washing.
Portland cement (finish mills)	Hydrocarbon	Reduce use of grinding aids.
Portland cement (kilns)	Condensed fume (alkali)	Reduce alkali recycle in insufflated dusts; use alkali bypass; change raw feed composition.
Municipal incinerators	Condensed fume (hydrocarbon)	Recycle waste and segregate before burning to remove plastics, metals, etc.; improve combustion.
Secondary metal furnaces	Hydrocarbons	Improve combustion; reduce oil/plastic content of charge; pre-burn charge.
Textile plants heat setting	Hydrocarbons	Pre-scour cloth; reduce fabric temperature.
Latex curing	Hydrocarbons	Improve purity of chemical agents; reduce usage; reduce curing temperature; change chemical formula.
Texturing	Hydrocarbons	Lower setting temperature; use oil of lower volatility; reduce usage.
Melt spinning	Hydrocarbons	Use less spin finish; change formula to reduce volatility; reduce temperature.
Residual fuel boilers	Acid aerosol	Reduce vanadium content of oil; reduce boiler excess air; improve soot blowing practices.

materials that are sticky or that agglomerate on the collection surface. Proper selection of abatement controls and careful management of gas stream and control device conditions can eliminate major problems in this area. Construcing ductwork control devices and waste systems from corrosion-resistant materials (fiber-reinforced plastic, Hastelloy) is one way to eliminate corrosion problems. Gas stream cooling has been applied effectively to several processes, including textiles, municipal incinerators, boilers, primary metals, specialty metals, and cement, kraft pulp, and refractory kilns.

3.4.2 Add-On Control Devices

Several add-on control options are available for collecting condensed aerosols (primary particulate and liquid aerosols). These include positive corona two-stage ESP's, ionizing wet scrubbers, high-energy venturi scrubbers, fabric filters, mist eliminators, dry ESP's, wet ESP's, and fume incinerators (direct-fired and catalyst). The application of each depends on process conditions, chemical species, separation of elements, particle size distribution, water vapor content, corrosive gases, and condensation temperature of aerosol. The principles and application of some of these control devices are described in detail in Appendix E.

3.4.3 Comparative Cost of Control Devices for Condensed Particulates

Table 5 presents the estimated costs of reducing condensed particulate emissions in five industries. These estimates are broad and may vary from plant-specific values.

TABLE 5. ESTIMATED TOTAL COST OF REDUCING CONDENSED PARTICULATE EMISSIONS
(September 1982 dollars)

Description	Filterable PM	Condensed PM
Coal-fired utility power plants		
$/kW	50.00	150.00
$/acfm	14.00	43.00
Efficiency, %	99.7	95.0
Wood-fired steam boiler		
$/acfm	2.00	20.00
Efficiency, %	90.0	90.0
Sinter stand (wind box)		
$/ton-year	4.00	7.50
$/acfm	15.00	30.00
Efficiency, %	99.0	95.0
Veneer dryers		
$/ft^2	0.0	190.00
$/acfm	0.0	5.00
Efficiency, %	N/A	95.0
Cement kiln		
$/ton-year	4.40	8.40
$/acfm	15.00	30.00
Efficiency, %	99.0	90.0

SECTION 4

CONDENSED PARTICULATE MATTER FROM MOBILE SOURCES

Some constituents of gaseous emissions from mobile sources condense to form particulate matter when cooled by dilution with ambient air. These emissions, consisting primarily of soluble organic fraction (SOF), vary substantially with engine type, fuel, and operating conditions, and are generally presented as a percentage of the total particulate mass. Mobile source emission factors currently used by EPA include condensed particulate. Soluble organics account for 10 to 60 percent of the total particulate mass emitted from mobile sources and occur predominantly in the respirable particulate size range (<10 µm).[19-21] Emission inventories show that mobile source exhaust contribute from 2.5 to 5.0 percent of calculated yearly particulate emissions.

Most studies concerning mobile source emissions categorize vehicles into two weight classes: light-duty and heavy-duty. Light-duty vehicles are those whose gross vehicle weight (GVW) is 8500 pounds or less; heavy-duty vehicles are those whose GVW exceeds 8500 pounds. Some studies reviewed for the purpose of this study also include a medium-duty class consisting of vehicles whose GVW ranges from 8500 to 10,000 pounds.

4.1 LIGHT-DUTY VEHICLES

The vast majority of light-duty vehicles are gasoline-powered. However, because diesels achieve higher MPG at the same vehicle weight than gasoline-powered vehicles, they are increasing in popularity. Unfortunately, diesel engines emit considerably more particulate matter than gasoline engines.

For light-duty vehicles using unleaded gas, the SOF varies from 5 to 23 percent; for vehicles using leaded gas the SOF varies from 9 to 30 percent, and for vehicles using diesel the SOF varies from 10 to 60 percent.[23,24] It should be noted, however, that these percentages can be misleading since the numbers indicate the condensed fraction of the total particulate emitted rather than the actual amount emitted. In fact, leaded gasoline engines emit from 3 to 10 times more total particulate matter per kilometer traveled than unleaded gasoline engines, while diesel engines emit approximately 20 times the amount of particulate matter per kilometer traveled as unleaded gasoline engines.[23,24] The amount of condensed particulate emitted per kilometer is the product of the percent SOF and the particulate emissions, specifically, 0.0015 to 0.0030 g/km for unleaded fuel, 0.013 to 0.050 g/km for leaded fuel, and 0.03 to 0.11 g/km for diesel fuel.[20, 23-25]

Experiments have been conducted recently to measure the effect of changing parameters such as engine load and mileage accumulation on the percent SOF. Generally, as the load increases, the total amount of material emitted increases, but the percent SOF drops for all types of engines. As mileage accumulates on light-duty diesel engines, the percent SOF increases for the first 32,200 km (20,000 miles) and gradually levels off for an indeterminate number of kilometers.[20] Data are not available on the effect of mileage accumulation on gasoline engines.

4.2 HEAVY-DUTY VEHICLES

Diesel engines presently power half of the heavy-duty vehicles and are preferred over gasoline engines because of their greater MPG and longer life, attributes that are expected to increase the number of diesel engines in this category faster than in the light-duty category. This increase also will be partly due to conversions from gasoline to diesel for compliance with 1983 heavy-duty gaseous emission standards. These emission standards may result in the use of catalytic converters on heavy-duty gasoline engines, which will in turn reduce the cost difference between gasoline and diesel engines and increase the use of diesel engines.

As mentioned earlier, although diesel engines give better mileage, they also emit substantially more total particulate matter than gasoline engines. The percent SOF for gasoline-powered heavy-duty engines is low, usually around 10 percent; the percent SOF for light- and heavy-duty diesel engines, on the other hand, can range from 10 to more than 60 percent.[25,26] For example, light-duty and heavy-duty diesels emit approximately 0.3 g/km and 1.0 g/km of total particulate matter, respectively. If 40 percent of this is assumed to be condensed particulate, this calculates to 0.12 g/km and 0.40 g/km of condensed particulate, respectively. When compared with the condensed particulate emissions from light-duty gasoline engines (0.003 g/km), condensed particulate emissions from heavy-duty diesel engines become significant. These vehicles contribute an estimated 50 percent of the mobile source TSP, whereas they account for only 4 percent of the vehicle miles traveled in an urban area.[27]

Several studies have been made on the effects of varying loads and fuel types on particulate emissions from heavy-duty diesel engines. In a study conducted by Dietzmann, Parness, and Bradow, three types of fuel were tested: minimum, average, and premium grades.[26] The results indicated that condensed particulate emissions changed as the grade of fuel changed; the emissions were 0.24 g/km, 0.26 g/km, and 0.29 g/km for minimum, average, and premium grades, respectively. The effect of varying driving conditions on particulate emissions was also tested and indicated that freeway driving conditions produced 40 to 55 percent of the total particulate emissions. In another study, a test of the effect of load on emissions demonstrated that as the load increased the percent SOF of the particulate matter decreased.[28]

4.3 TEST METHODS FOR MOBILE SOURCES

It should again be noted that the current EPA mobile source emission factors include condensed particulate matter. The testing program for mobile sources is discussed in more detail in Appendix E. The principle of this sampling system is similar to that of the SDSS. Of all the sampling parameters, the amount of dilution air used and the temperature of the collection filter have the greatest effect on the formation of condensed particulate matter. Any dilution in excess of 10 parts dilution air to 1 part source effluent provides reproducible results. The filter temperature affects sampling since the greater the filter temperature, the lower the condensed particulate matter.

4.4 MOBILE SOURCE IMPACT IN AN URBAN SITUATION

Established methodologies exist for modeling mobile source emissions from specific points or roadways. Attempting to model mobile source emissions in a large urban area is more complex, however, and less well defined. A large percentage of mobile source emissions occur in urban areas. Typical TSP contributions from mobile sources in a central business district average

10 to 11 $\mu g/m^3$, of which an estimated 25 percent represents condensed particulate matter.[28] Additional information is needed on the concentration distribution of condensed particulate matter and its impact on the urban area.

Bradow conducted a particulate exposure analysis in which 1985 exposures were calculated in St. Louis, Missouri, by using the Gaussian-plume multiple-source air quality algorithm (RAM) model.[29] St. Louis was selected for this analysis because extensive data were available as a result of EPA's Regional Air Pollution Study (RAPS). The RAM model predicted TSP contributions of 13 $\mu g/m^3$ from mobile sources in the central city area, which decreased to 6 $\mu g/m^3$ and 2 $\mu g/m^3$ in residential and suburban areas, respectively. When comparing these data to a 1977 emission inventory, Bradow concluded that mobile sources contribute approximately 15 percent of the fine fraction of ambient aerosols in St. Louis. It should be noted that diesel engines are currently the principal source of fine particulate and that the number of diesels is slowly increasing.

Although the areawide contribution of mobile sources is small compared with the contribution of other source categories, the air quality impact on a limited geographic area is significant. Because mobile sources emit their pollutants in proximity to population centers, the local concentration of fine particulate matter from mobile sources can reach levels close to 100 $\mu g/m^3$ under adverse meteorological conditions.[29]

4.5 FUTURE MOBILE SOURCE TRENDS

Over the last several years regulations have been promulgated that specify the average miles per gallon light-duty vehicles must achieve and their allowable emissions. These regulations are based on current available technology, economic feasibility, and forecasts of future trends in vehicle use and technology. Assuming constant emissions per vehicle, the forecasts indicate a substantial increase in condensed particulate matter emissions in the future.

Projections indicate that 25 percent of the vehicles produced by one American corporation in 1985 will be light-duty diesels, and by 1995, diesel engines will comprise 25 percent of the total U.S. sales. Several factors could affect these estimates and result in ranges of diesel sales from 10 to 50 percent. Factors such as technological feasibility and regulatory changes will determine the exact amount of the growth of this class and type of vehicle. Light-duty diesel engines produce approximately 20 times more condensed organics per vehicle kilometer than light-duty unleaded-gasoline engines. As diesel-powered vehicles increase in number and replace gasoline-powered vehicles, the emissions of condensed organics will increase significantly. Assuming that the emissions per vehicle remain constant, nationwide annual condensed organic emissions from light-duty diesels will increase from 0.1×10^3 to 38.9×10^3 Mg/yr in 1995.[22]

Heavy-duty vehicles, currently half gasoline-powered and half diesel-powered, are projected to become totally diesel-powered by 1995.[22] Currently, heavy-duty diesels emit 29.4×10^3 Mg/yr of condensed organics, whereas heavy-duty gasoline engines emit 5.9×10^3 Mg/yr. Emissions from a heavy-duty diesel can be as much as 10 times higher than those from a heavy-duty gasoline engine, but this value varies considerably.[25] Therefore, assuming that 100 percent of the heavy-duty vehicles are converted to diesel engines, condensed particulate emissions from the heavy-duty vehicles category could potentially increase to 58.8×10^3 Mg/yr.[22]

If both of the previous predictions are accurate (i.e., the nationwide conversion of 25 percent of light-duty vehicles and 100 percent of heavy-duty vehicles to diesels), condensed particulate emissions could increase from 67.9×10^3 to 97.7×10^3 Mg/yr.

SECTION 5

CASE STUDIES OF POTENTIAL CONDENSED PARTICULATE MATTER EMISSIONS IN THREE CITIES

As part of this study, three urban areas (Houston, Texas; Philadelphia, Pennsylvania; and Portland, Oregon) were analyzed to determine the increase in primary particulate emissions if condensed particulate matter for certain stationary sources was to be included in the emissions inventories of heavy population centers. The primary criterion for selecting these three study areas was data availability, which also determined the extent of detail of the analyses. Emission inventories were examined and calculated condensed particulate emission factors (from Section 4 of this report) were applied to the various stationary source categories. All these sources were assumed to be controlled. The generated values were presented earlier in Table 2.

5.1 HOUSTON, TEXAS

Data from EPA's 1980 visibility and characterization experiment in Houston were analyzed to determine the potential effect of condensed particulate emissions on the Houston-Galveston urban area.[30] Sources emitting 100 tons/yr or more of particulate matter were tabulated from a 1973 NEDS inventory. The Texas Air Control Board (TACB) then determined the maximum emission potential of each source type according to permit applications for point sources with the potential to emit at least 200 tons/yr.

Fluid crackers in the petroleum industry accounted for 23 percent of total 1973 particulate emissions, followed by natural gas combustion at 19 percent. Since 1973, a large increase in emissions from fuel oil combustion has been permitted, along with substantial increases in emissions from natural gas combustion. These source categories are believed to contribute significant condensed particulate emissions to the ambient air. Condensed particulate matter forms in the respirable size range, generally with diameters less than 1 μm. Table 6 presents the 1973 NEDS point source inventory data for the Houston-Galveston urban area, along with estimates of potential condensed particulate emissions extrapolated from the back half emission factors calculated

TABLE 6. 1973 STATIONARY SOURCE PARTICULATE MATTER, ESTIMATED CONDENSED PARTICULATE, AND ESTIMATED TOTAL PARTICULATE EMISSIONS FROM SOURCE TYPES IN THE HOUSTON-GALVESTON URBAN AREA THAT GENERATE GREATER THAN 100 TONS/YEAR
(tons/year)

Source type	1973 PM emissions[a]	Estimated emissions Condensed PM	 Total PM
Fluid catalytic crackers	11,017	3,460	14,477
Natural gas combustion (including boilers, process heaters, cement kilns)	8,997[b]	NDA[c]	-
Fertilizer production	3,337	2,466	5,803
Rock handling--quarries, (including storage, crushing, grinding, etc.)	2,898	NC	2,898
General sintering--iron production	2,349	969	3,318
Grain handling	1,973[b]	NDA	-
Wood bark boiler	1,910	365	2,275
Electric arc furnace--steel production	1,315	310	1,625
Residual oil boilers	1,141	1,531	2,672
General polymer production	1,116[b]	NDA	-
Recovery boiler--sulfate pulping	1,034	173	1,207
Ferromanganese furnace	890[b]	NDA	-
Oil petroleum process heater	846	1,009	1,855
Distillate oil boilers	827	1,110	1,937
Liquor oxidation tower--sulfate pulping	820[b]	NDA	-
Miscellaneous industrial incinerators	742	1,362	2,104
Material handling--cement manufacturing	681	NC[d]	681
Iron--direct reduction	641	151	792
Silico--manganese ferroalloy open furnace	621[b]	NDA	-
Miscellaneous crude fractionation and aromatic recovery	564[b]	NDA	-
Material handling--brick manufacturing	554	NC	554
Sulfuric acid contact	513[b]	NDA	-
Flare	430[b]	NDA	-

(continued)

TABLE 6 (continued)

Source type	1973 PM emissions[a]	Estimated emissions Condensed PM	Total PM
Blast furnace fugitive emissions	340	80	420
General PVC production	314[b]	NDA	-
Asphalt applications	253	120	372
Coke quenching	238[b]	NDA	-
Calcining--time production	228	26	254
Sulfate pulping	210	53	263
Tin blast furnace	175[b]	NDA	-
Tetraethyl lead manufacturing	154[b]	NDA	-
Saw mill	153	14	167
Calcining	146[b]	NDA	-
PVC calendaring	132[b]	NDA	-
Coal crushing/handling	106	NC	106
Lime kilns--sulfate pulping	106	68	174
Smelt dissolving tank--sulfate pulping	102	20	123
Totals	30,790	13,287	44,083

[a] From 1973 NEDS emission inventory.

[b] Not included in total since no data were available.

[c] NDA = no data available.

[d] NC = no condensed particulate.

in Section 4 of this report. Table 7 presents the maximum potential for emissions based on post-1973 permit data. Both studies were of the urban area only and may not represent the AQCR.

TABLE 7. STATIONARY SOURCE PARTICULATE MATTER, ESTIMATED CONDENSED PARTICULATE, AND ESTIMATED TOTAL PARTICULATE EMISSIONS IN THE HOUSTON-GALVESTON URBAN AREA, BASED ON TACB PERMIT APPLICATIONS AFTER 1973 (tons/year)

Source type	Maximum PM emissions[a]	Estimated emissions Condensed PM	Estimated emissions Total PM
Fuel oil combustion	13,674	18,349	32,023
Natural gas combustion (including boilers, process heaters, cement kilns)	5,109	563	5,672
Coal combustion	2,509	277	2,786
Trench burners	2,496[b]	NDA	-
Olefins production	1,410[b]	NDA	-
Fluid crackers	1,183	372	1,555
Vinyl chloride production	440[b]	NDA	-
Continuous casting--steel	438[b]	NDA	-
Hydroforming	298[b]	NDA	-
Rock crushing	201	NC	201
Totals	22,676	19,561	42,237

[a] Includes point sources with potential to emit at least 200 tons/yr.

[b] Emissions are not included in the total since no data were available.

In the categories for which it was possible to make estimates, the total condensed particulate matter is estimated to be 13,287 tons/yr, as shown in Table 6.

Based on 1973 data, the current particulate emissions inventory from stationary sources in the Houston-Galveston urban area would have to be increased by 43 percent if the estimated condensed particulate sources were to be included in the inventory; the TACB study would be increased by about 88 percent.[29]

Unfortunately, the data were inadequate to relate air quality to the emission estimates on a source-specific basis, i.e., to estimate the impact on a particular monitoring site.[30]

5.2 PHILADELPHIA, PENNSYLVANIA

To determine the potential effect of condensed particulate emissions on the Philadelphia airshed, a summary of point source emissions from the NEDS inventory was analyzed by using the emission factor technique discussed earlier in this section. These data were summarized as part of a neighborhood-scale study of inhalable and fine suspended particulate matter conducted in Philadelphia in 1980.[31] Table 8 presents these neighborhood emission data, estimated condensed particulate emissions, and total particulate emissions including the condensed particulate portion. (This neighborhood-scale study may not represent the AQCR.) If insufficient information was available concerning the actual source type (e.g., chemical production), no emission factor was applied to that source category. Table 8 shows that in the categories for which it was possible to make such an estimate, the total condensed particulate is estimated to be 3873 tons/yr. This value is probably biased high in relation to the impact on TSP because of the major categories for which condensed particulate emissions are estimated. Most of these sources are subject to artifact formation in the modifed Method 5 test on which the emission factors are based.[32] However, residual oil combustion--the primary source category in the Philadelphia airshed--accounts for 21 percent of the total NEDS source category emission rates that are greater than 5 tons/yr.

The current particulate emissions inventory for stationary sources in the Philadelphia neighborhood-scale study would increase by 92 percent if potential condensed particulate sources were to be included in the inventory. Unfortunately, as noted in Section 5.1, the data were inadequate to relate air quality to the emissions estimate on a source-specific basis.

5.3 PORTLAND, OREGON

The Portland Aerosol Characterization Study (PACS) identifies major sources of both TSP and respirable particulate (<1 μm) in the Portland-Vancouver interstate air quality maintenance area.[33]

The methodology of PACS was to analyze the ambient particulate matter collected and attempt to account for the original source rather than estimating the impact on the ambient monitor. The contributions of condensed particulate, although not identified, were accounted for in PACS because of the methodology applied.

TABLE 8. STATIONARY SOURCE AND ESTIMATED CONDENSED PARTICULATE EMISSIONS IN PHILADELPHIA NEIGHBORHOOD SCALE STUDY (tons/year)

Source type	Inhalable and fine particulate emissions study[a]	Estimated emissions	
		Condensed PM	Total PM
Residual oil combustion	987	1748	2735
Refinery oil heater	726	866	1592
Municipal incinerators	705	306	1011
Anthracite coal combustion	651	723	1374
Coke oven	466	184	650
Feed and grain handling	404	NC	404
Chemical preparation	109[c]	NDA	-
Mineral handling	108	NC	108
Copper smelting	96[c]	NDA	-
Sugar cane processing	94[c]	NDA	-
Natural gas combustion	51	NDA	-
Can label coating oven	50[c]	NDA	-
Cargo handling	44	NC	44
Paint production	44[c]	NDA	-
Asphaltic roofing materials products	41	32	73
Forest products	34[c]	NDA	-
Zinc galvanizing	29[c]	NDA	-
Carpet making	23[c]	NDA	-
Carbon black furnace	12[c]	NDA	-
Aluminum melting furnace	7	14	21
Lead smelting	5[c]	NDA	-
Totals	4319	3873	8012

[a] Sum of all NEDS emission rates greater than 5 tons/yr within a source category from Philadelphia and Camden Counties. (Reference 31)

[b] NC = no condensed PM emitted; NDA = no data available.

[c] Emissions are not included in totals since no data were available.

Available data for Portland identified about 90 percent of the sources of TSP and only 65 percent of the sources of respirable particulate. Background sources contribute 40 percent of Portland's TSP and 49 percent of the respirable particulate.[33] Table 9 lists the major sources of locally generated TSP. This study was of the Air Quality Maintenance Area (AQMA) and may not represent the AQCR. Condensed particulate contributions are calculated by using the emission factor technique described in Section 5.1. The source inventory, although not used quantitatively in the study, was used qualitatively to identify candidates for characterization and inclusion for the receptor model. Table 10 presents the PACS estimate of fine particulate matter emissions in the Portland airshed by source category.

In stationary source types for which it was possible to make an estimate, the total condensed particulate is estimated to be 1349 tons/yr. When compared with the total of all other primary particulates (11,046 tons/yr), this value indicated that the data base should have accounted for an additional 11 percent of condensed particulate. The same condensed particulate value, when compared with the fine particulate (<10 μm) data base (Table 10), indicated that the stationary source was emitting an additional 18 percent condensed particulate matter. This increase in the fine particulate data base seems to be very low, and the impact on fine particulate would be expected to be at least twice the value shown in Table 10. The Portland data are believed to be biased low because some of the sources were not included in the inventory. Among those sources not accounted for are hog fuel boilers and aluminum smelters, which are believed to be significant contributors of condensed particulate. Also, the major source of Portland's locally generated TSP is geological dust (e.g., road dust), which accounted for 24 percent of the TSP in 1977-1978. No condensed particulate emissions are expected from this source category. Potential industrial sources of condensed particulate contributed only 2 percent of the TSP in downtown Portland. Stationary sources contributed about half of the total annual emissions in Portland. Therefore, the impact on annual emissions from stationary sources would be increased only by 22 percent by the inclusion of condensed particulate. This percentage of condensed particulate contribution is low compared with the 30 percent and 48 percent in Houston and Philadelphia, respectively.

---

[a] Since the particle cut size varied between studies for fine particulate, the particle size will be given for each fine particulate study.

TABLE 9. ESTIMATED TOTAL PARTICULATE EMISSION RATES IN PORTLAND AIRSHED[a]

Source category	Annual emissions,[b] tons/yr	Percent of total in Portland[c]	Annual condensed PM emissions,[d] tons/yr	Total emissions, tons/yr
Geological	4,411	26.1	22	4,433
Transportation[e]	3,688	21.8	-	3,688
Fossil fuel	815	4.8	857	1,672
Vegetative burning	488	2.9	-	488
Forest product industry	3,255	19.1	183	3,408
Vegetative	568	3.4	187	755
Aluminum industry	1,650	9.8	-	1,650
Iron industry	261	1.5	52	313
Miscellaneous stationary sources	1,807	10.7	48	1,855
Totals	16,913	-	1,349	18,262

[a] PACS.

[b] Based on reference method test data.

[c] Percentage does not include condensed particulate.

[d] Represents condensed particulate from stationary sources only.

[e] The condensed particulate is part of the mobile source emissions data.

TABLE 10. RELATIVE CONTRIBUTION OF CONDENSED PARTICULATE MATTER TO FINE PARTICULATE IN PORTLAND

Source category	Annual emissions,[a] tons/yr	Percent of total emissions	Annual condensed PM emissions, tons/yr	Total emissions, tons/yr
Geological	495	5.7	22	517
Transportation[b]	1,938	22.5	-	1,938
Fossil fuel	781[c]	9.1	857	1,638
Vegetative burning[d]	395	4.6	-	395
Forest product industry	2,197[c]	25.5	183	2,380
Vegetative	271[c]	3.1	187	458
Aluminum industry	1,023[c]	11.9	-	1,023
Iron industry	211[c]	2.4	52	263
Miscellaneous stationary sources	1,312[c]	15.2	48	1,360
Totals	8,623	-	1,349	9,972

[a] PACS.

[b] Condensed particulate matter not shown because the test method accounted for it.

[c] Total emissions for process where relationship with condensed particulate matter is known.

[d] Emissions estimated from DEQ report.

SECTION 6

EFFECT OF CONDENSED PARTICULATE ON AMBIENT PM_{10}

It is difficult to establish a quantitative impact of condensed particulate on PM_{10}. Because condensed particulates form in the submicrometer particle size range, these particulates would have an impact on an ambient monitoring site, but at this time it is difficult, if not impossible, to differentiate between primary and secondary particulates when analyzing ambient monitoring site results.

An additional effect of condensed particulates on the atmosphere is the impairment of visibility. Although the extent of this visibility impairment is unknown, some preliminary work in Houston and Detroit lends itself to a qualitative discussion.

6.1 PRIMARY AND SECONDARY PARTICULATES STUDIES

Studies of the particulates released by coal combustion have shown the existence of two distinct size modes on a mass basis.[34,35] The first occurs at particle sizes of 0.1 µm in diameter and the second at particle sizes larger than 0.5 µm. The mode at the 0.1 µm diameter size apparently results from volatilization of ash components during combustion and subsequent nucleation, coagulation, and condensation of the volatilized components as the combustion gases cool. This is borne out by the preferential concentration of the more volatile elements measured on the smaller sized particles.

Other studies of power plant plumes have shown that 90 percent of a unit's primary sulfate emissions were in the entrained scrubber liquor.[36] In this study, primary sulfates accounted for 4 to 17 percent of total sulfates measured downwind in the plume.

Once released, primary pollutants are subject to atmospheric chemical and physical processes in their transformation to secondary pollutants. The percentage of gas-to-particle conversion product that forms new particles (nucleation) has been reported to average between 5 and 10 percent for power plant plumes.[37,38] Thus, condensation apparently accounts for most of the particle growth in power plant plumes. Conversion of SO_2 to secondary particulate sulfate in these plumes ranges from 0 to 10 percent per hour, depending on a number of variables.[36,37,39] This conversion rate appears to be heavily influenced by photochemical processes.

A recent study estimating the primary sulfate formation from fossil fuel-fired combustion sources was performed by oxygen isotope ratio measurements.[40] This study compared the oxygen isotope ratios ($^{18}O/^{16}O$) in sulfate compounds found in the atmosphere with isotope ratios in the boiler stacks.[40] The basis for the ratio estimates is that the sulfates formed from combustion gases is higher in ^{18}O than sulfates formed in the atmosphere as a result of atmospheric reactions of the SO_2 emitted from the source. This study estimated that 10 to 40 percent of the sulfates emitted from the sources tested were primary sulfate.[40] It should be noted that the authors of this study defined primary sulfate as that sulfate formed only from gases exiting the combustion sources. Unlike the definition of primary sulfate used in this report, their definition did not allow for sulfates formed with entrained air immediately after leaving the stack (Section 2). Based on this referenced study, it could be concluded that more than 10 to 40 percent of the ambient sulfate particulate matter was emitted as a primary sulfate from a combustion source rather than a secondary conversion to sulfur dioxide. This analytical method may find application for estimating primary and secondary sulfate formation for fossil fuel-fired steam generators in general.

6.1.1 Ambient Studies

On the average, 30 percent of the aerosol mass in Los Angeles results from gas-to-particle conversion in the atmosphere.[41] Estimates of 15 to 20 percent primary and 30 to 40 percent secondary organic carbon have been made at Pasadena, Pomona, and Riverside.[14] During a severe photochemical episode in Pasadena, secondary material (organics, nitrates, and sulfates) has accounted for 95 percent of the total aerosol mass.[39]

Primary organics include linear and branched alkanes and alkenes, substituted benzenes and styrenes, quinones, acridines, quinolines, phenols, cresols, phthalates, fatty acids, carbonyl compounds, some pesticides, and polycyclic aromatic hydrocarbons (PAH's).[41] Secondary organics are too numerous to mention, but most are difunctional in nature, which results in a marked decrease in the vapor pressure of the secondary organic relative to that of a precursor primary organic of similar carbon number. This also probably accounts for the efficient aerosol formation capability of secondary organics.

In both ambient air and power plant plumes a major portion of sulfates is found in the fine particle fraction (0.5 μm). Ambient suburban samples have shown that 85 to 90 percent of aliphatic acids, 90 to 95 percent of carboxylic acids, and 95 to 98 percent of PAH are found on particles with diameters of less than 3 μm.[42] Seventy-five and 85 percent of the mass of the two PAH's, benzo(a)pyrene and coronene, were found to be associated with particles with diameters of less than 0.26 μm.[43] Thus, in ambient air, a substantial portion of both sulfates and particulate organic carbon is found in the fine particle fraction below 0.5 μm in diameter.

6.1.2 Models

Source-oriented atmospheric dispersion modeling has been used to attribute ambient pollutant concentrations to source emissions.[44,45] Using high-quality emission inventories and representative meteorological information, these models have often been able to make adequate predictions of the specific sources of nonreacting gaseous pollutant concentrations at receptors. These source models have proved to be inadequate for predicting particulate matter concentration, however, for the following reasons:

- Particulate emissions are widely dispersed (arising from both point and area sources) and difficult to quantify.
- Transport of particulate matter is strongly dependent on particle size.
- Standard source models are not equipped to deal with the complexities of aerosol chemistry and physics.

Whereas source-oriented models begin with measurements at the source and estimate ambient concentrations, receptor-oriented models begin with ambient concentrations and estimate source contributions to them. The receptor model relies on properties of the aerosol that are common to source and receptor and are unique to specific source types, such as composition, size distribution, and variability (due to variation at the source and to meteorological transport). Currently used receptor models can be classified as chemical-mass-balance, multivariate, microscopic, and hybrid source/receptor. Regardless of the type of receptor model used, however, aerosol composition, size, and variability data are needed at both source and receptor for these models to work. Lack of adequate source sampling and characterization appears to be the major limitation to advancing the application of receptor modeling.

Since neither source nor receptor models are entirely satisfactory for defining the source-receptor relationship of particulate pollutants, distinguishing primary from secondary particulates would appear to present an even more formidable task. For example, transformation rates may differ for different sources (given particulate species may exist within an airshed as both primary and secondary particulate), and certain sources may not be associated with unique secondary particulates. This suggests that except on a case-by-case basis where a special field study has been carried out, it would be difficult to take ambient particulate data (such as HIVOL), separate the primary from the secondary particulates, and then reconcile them to their respective sources.

6.2 VISIBILITY IMPAIRMENT

Although the mechanisms of human perception and the fundamentals of atmospheric visibility impairment are understood reasonably well, some uncertainties remain. Visibility impairment results from light scattering and absorption by particles (mostly fine) and, to a lesser extent, NO_2. Principal categories of impairment include 1) plume blight near sources, 2) bands or layers of discoloration or veiled haze, and 3) widespread regionally homogeneous haze. Important causes of impairment include natural sources (blue sky scatter, fog, dust, forest fires, volcanoes, sea spray, and biologic sources) and manmade sources of sulfur oxides, particulates, nitrogen oxides, and volatile organics. Important source categories of visibility impairment include utilities, industrial fuel combustion, smelters, pulp mills, urban plumes, fugitive dust, and managed fires. A number of empirical techniques have been developed for identifying sources of observed impairment. Visibility models are being validated and should be used to evaluate the impact of point sources at distances of up to 150 km from the sources. Regional models are useful for analyses, but they require further refinement before regulatory application.[46]

Condensed particulate matter contributes to visibility impairment for several reasons. First, condensed particulate forms in the submicrometer size range and scatters or absorbs light. Second, some reactions taking place in the atmosphere lead to secondary product formation from some condensed particulate, such as sulfuric acid mist, which forms more light scattering or absorbing products.[47] Therefore, the potential for visibility impairment is present where there are sources of condensed particulate. Because this report is oriented toward the urban situation, the discussion of visibility impairment centers on urban visiblity.

Visibility impact in urban areas varies with source composition, meteorology, location, and season. The principal sources of primary and secondary fine aerosols are 1) major stationary source emissions of sulfur oxides, organics, and primary particulate matter, 2) mobile source emissions, and 3) space heating. Many of these sources also emit nitrogen oxides.

Among the point sources potentially important to visibility impairment are utilities, industrial fuel combustion pulp mills, and smelters. These point sources are significant contributors to condensed particulate, and the condensed particulate, in turn, is related to visibility impairment. Studies on the effect of visibility impairment by aerosol formation and fine particulate were conducted in Houston, Texas, and Detroit, Michigan.[48,49] Although these studies did not differentiate condensed particulate from other fine particulate, they did identify some chemical species that could have originated as condensed particulate.

Figure 3 shows the makeup of the fine fraction (<2.5 μg) of particulate matter found in the Houston study.[48] The largest portion (sulfates) was found to be associated predominantly with ammonium sulfate mixed with 19 percent sulfuric acid in the day and 7 percent at night.[48] It was also concluded from ^{14}C data that 60 ± 15 percent of the carbon in the fine fraction originated from fossil fuel combustion. The apportionment of mean daytime light extinction coefficient (a measure of visibility impairment) was as follows: 4.7 percent by nitrogen dioxide gas, 32 percent by sulfate and related cations, 17 to 24 percent by carbon, 5 percent by other species, 16 percent by water evaporated from these particles, 13 ± 7 percent by bound water, and 5.6 percent by the ambient air (normal molecular makeup).[48]

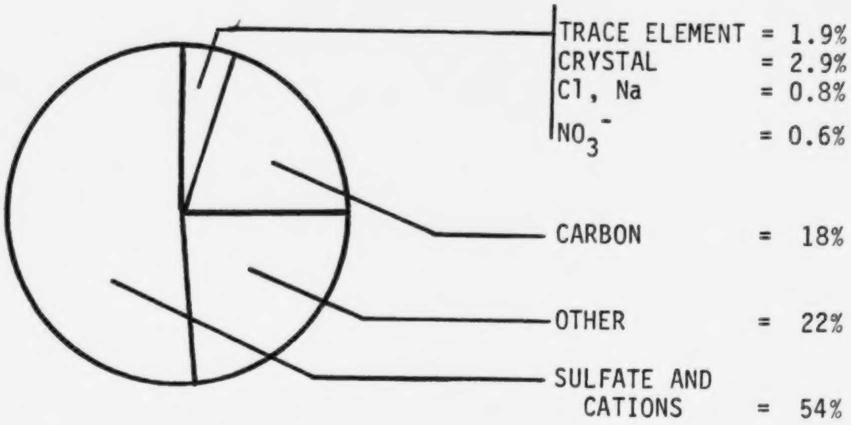


Figure 3. Eight-day average of daytime fine- and coarse-fraction mass concentrations apportioned by chemical species in Houston from September 11 to 19, 1980.[48]

The quantitative estimate of condensed particulate contributing to visibility impairment in Houston could not be determined, but a qualitative statement can be made to the effect that a large portion of the species was probably condensed particulate in origin.

The Detroit study[49] found visibility impairment to be due to the same chemical species as those found in the Houston study.[48] As would be expected, the proportions of the chemical species were comparable, but not the same, because the source contributors are different in the two areas. Figure 4 shows the contribution to the mean daytime light extinction coefficient. In the Detroit study, the dominant chemical species was ammonium sulfate, which accounted for about 50 percent of the fine particulate.[49] This study also showed that sulfates are the most efficient light-scattering fine particles per unit mass of dry weight.[49]

As in the Houston study, it was not possible to arrive at a quantitative estimate of the condensed particulate contributing to visibility impairment in Detroit, but a qualitative statement can be made to the effect that a large portion of the species was probably condensed particulate in origin.

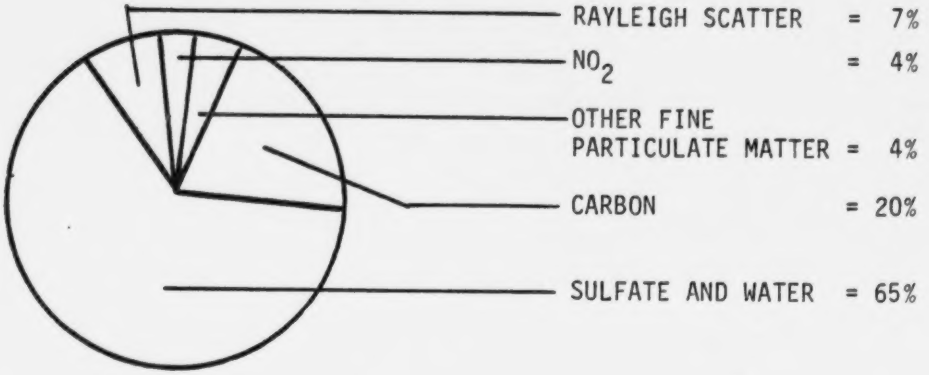


Figure 4. Contributions to the mean daytime light extinction coefficient in Detroit (July 15 to 21, 1981).[49]

6.3 IMPACT BASED ON NATIONAL EMISSIONS DATA REPORTS

In Section 5, the impact of total primary particulate from selected stationary sources was estimated to be 30 percent condensed particulate in Houston, Texas; 48 percent in Philadelphia, Pennsylvania; and 22 percent in Portland, Oregon. Two data reports were adjusted to estimate the percent contribution of condensed particulate to primary particulate emissions on a national basis. Table 11 shows the 10 major contributors to TSP as reported by OAQPS and the corresponding source-specific condensed particulate emissions. These adjusted results indicate that condensed particulate would contribute about 27 percent of the total primary particulate impact on TSP. Table 12 shows the 10 largest stationary source particulate emitters as reported by DSSE in 1978. These adjusted results indicate that condensed particulate would contribute about 30 percent of the total primary particulate impact on TSP from stationary sources only. This computation is based on various assumptions that may not be valid, but it does serve as an estimate.

6.4 RECOMMENDATIONS FOR FUTURE STUDY

There are two basic weaknesses in the data used in this report. The first weakness deals with the use of data from the back half of the EPA Method 5 source tests. As noted previously, Method 5 tests are subject to artifact formation and other errors that make it difficult to use these data

TABLE 11. MAJOR SELECTED SOURCE CATEGORIES EMITTING CONDENSED PARTICULATE

Source category	TSP, [x 10^3 tons]	Condensed particulate, [x 10^3 tons]	Total, [x 10^3 tons]
Integrated iron and steel plants and coke ovens[a]	3388	1164.0[b]	4552.0
Portland cement plants	981	271.4[c]	1252.4
Coal-fired electric utility boilers	966	768.3	1734.3
Coal-fired industrial boilers	831	91.6	922.6
Kraft pulp and paper mills	297	89.7[b]	386.7
Asphalt batching plants	164	77.4	241.4
Primary nonferrous smelters	142	56.9[d]	198.9
Grey iron foundries	134	41.4	175.4
Lime plants	168	15.3	183.3
Total	7071[e]	2576	9647

[a] Includes emissions from material handling and storage piles.

[b] Average of aggregate emissions.

[c] Weighted average (25% wet process; 75% dry process).

[d] Weighted average based on production (54% Cu; 19% Pb; 22% Zn; 5% other).

[e] OAQPS data file of Nationwide Emissions, 1978, was adjusted for revised iron and steel emission factors projected to 1979 on basis of GNP growth.

TABLE 12. STATIONARY SOURCE CATEGORIES ACCOUNTING FOR TWO PERCENT OR MORE OF 1978 ACTUAL PARTICULATE EMISSIONS

Source category	Percent of total actual emissions	Percent after adjustment for condensed PM
Coal-fired steam electric power plants	19.1	34.4
Stone and rock processors	10.9	10.9
Portland cement plants[a]	6.3	10.7
Coal-fired industrial boilers	5.6	6.2
Iron and steel mills and coke plants	6.7	9.6
Grain elevators and mills	5.5	7.4
Forest fires and prescribed burning[b]	4.2	4.2
Solid waste disposal	3.5	5.0
Brick and tile plants	2.9	4.0
Primary copper smelters	2.6	4.3
Total	67.3%	96.7%

[a] Weighted average (25% wet process; 75% dry process).

[b] Condensed particulate concentration was unknown; therefore it is not included.

to estimate condensed particulate. The second weakness deals with the current ambient air quality data and the ability to relate emissions to air quality.

With regard to the first weakness, more source testing needs to be performed on stationary sources to establish more reliable emission factors for condensed particulate matter. This testing should be conducted using the SDSS train discussed in Appendix E of this report.

With regard to the second weakness, the relationship between primary and secondary sulfate formation should be more closely investigated. In the cities of Detroit and Houston more than 50 percent of the fine particulate matter (<2.5 μm) was made up of sulfate compounds. Additional studies similar to that conducted by Holt[40] on fossil fuel-fired steam generators and primary sulfate formation are recommended. Once the relationship between primary and secondary sulfate formation has been established, a dispersion model such as the Industrial Source Complex-Short Term (ISC-ST) can be used with the appropriate conversion rates for secondary sulfate formation to estimate the impact of condensed particulate matter on air quality. Receptor modeling techniques should also be developed to consider condensed particulate matter.

Finally, a coordinated program to relate receptor modeling to ambient air quality analyses should be implemented. Monitoring networks should be established based on the projected impact from selected sources. Tracer studies or the oxygen isotope ratio method described in Section 6.1 (for combustion sources only) can be used to determine the condensed particulate matter contribution at the established receptor locations. The monitoring program should be designed to provide information on the amount of particulate formed as a result of primary and secondary formation.

REFERENCES

1. U. S. Environmental Protection Agency. Emission Reduction Study - Stationary Source of Air Pollution (1970-79). Final Report. EPA-340/1-81-001, February 1981.

2. Massagolia, M. F., J. P. Wood, and K. H. Babb. Emission Reduction Study Stationary Sources of Air Pollution (1970-1979). Research Triangle Institute, Research Triangle Park, North Carolina. EPA-340/1-81-001a, February 1981.

3. Blagun, B., and D. Dunbar. Compilation of Ambient Particulate Matter Size and Composition Data. PEDCo Environmental, Inc. Contract No. 68-02-3512, Task No. 10. January 1982.

4. Personal communication. Discussions with ESRL personnel, June 1982.

5. U.S. Environmental Protection Agency. Air Quality Criteria for Particulate Matter and Sulfur Oxides. External Review Draft No. 1. April 1980.

6. Whitby, K. T., R. B. Husar, and B. Y. Liu. The Aerosol Size Distribution of Los Angeles Smog. Journal of Colloid and Interface Science, 39:177-204, 1972.

7. Husar, R. B., and K. T. Whitby. Growth Mechanisms and Size Spectra of Photochemical Aerosols. Environmental Science and Technology 7:241-247, 1973.

8. Hindman, E. E., P. V. Hobbs, and L. F. Radke. Journal of the Air Pollution Control Association, 27:(3)224-229, 1977.

9. Egan, R. C., P. V. Hobbs, and L. F. Radke. Journal of Applied Meteorology, 13:(8)535-552, 1974.

10. PEDCo Environmental, Inc. Identification of Parameters that Affect the Particulate Emissions From Kraft Recovery Boilers. U.S. EPA Contract No. 68-02-3546, Task No. 9. June 1982.

11. Personal communication from R. Hawks, PEDCo Environmental, Inc., Durham, North Carolina, October 1, 1982.

12. Armstrong, J. A., et al. Balloon-Borne Particulate Sampling of the Glen Falls Portland Cement Plant Plume. Denver Research Institute, University of Denver, Denver, Colorado. EPA Grant No. R805926-01, July 16, 1974.

13. Grotecloss, G., et al. NH_3 Effects in Cement Kiln Plume Formation and in SO_2 Determinations. Northrop Services, Inc., Research Triangle Park, North Carolina. U.S. EPA Contract No. 68-02-2566. July 1979.

14. Green, H. L., and W. R. Lane. Particulate Clouds: Dusts, Smokes and Mists. E and F. N. Spon Ltd., London. 1964.

15. Research Triangle Institute. Screening Study on the Justification of Developing New Source Performance Standards for Various Textile Processing Operations. U.S. EPA Contract No. 68-02-0607-11. August 1974.

16. Hawks, R. L. Hydrocarbon Carrier Emissions from Atmospheric Dye Becks. Presented at the U.S. EPA Emission Inventory/Factory Workshop, Raleigh, North Carolina, September 13-15, 1977.

17. North Carolina Department of Natural and Economic Resources, Division of Environmental Management, Air Quality Section. Biphenyl Emission Test Report for Loop Dryer #3, Wake Finishing Plant, Burlington Industries. July 22 and 24, 1975.

18. Hawks, R. L. Ambient Air Study of Benzene Soluble Organic Particulates Near Textile Wet Processing Facilities. Final Report. North Carolina Department of Natural and Economic Resources, Division of Environmental Management, Air Quality Section. June 1976.

19. Plee, L. S., and J. S. MacDonald. Some Mechanisms Affecting the Mass of Diesel Exhaust Particulate Collected Following a Dilution Process. SAE Technical Paper, No. 800186. 1980.

20. Gibbs, R. E., J. D. Hyde, and S. M. Byer. Characterization of Particulate Emissions From In-Use Diesel Vehicles. SAE Technical Paper No. 801372. 1980.

21. Ingalls, M. N., and R. L. Bradow. Particulate Trends with Increasing Dieselization. Presented at the 1981 Air Pollution Control Association Annual Meeting, Philadelphia, Pennsylvania.

22. Chapter 5: National Impact of Motor Vehicle Particulate Emissions.

23. Hare, C. T., and F. M. Black. Motor Vehicle Particulate Emission Factors. Presented at the Air Pollution Control Association 74th Meeting and Exposition, June 21-26, 1981.

24. Lang, J. M., et al. Characterization of Particulate Emissions from In-Use Gasoline-Fueled Motor Vehicles. SAE Technical Paper. No. 811186. 1981.

25. Dietzmann, H. E., M. A. Parness, and R. L. Bradow. Emissions from Gasoline and Diesel Delivery Trucks by Chassis Transient Cycle. ASME No. 81-DGP-6, 1981.

26. Dietzman, H. E., M. A. Parness, and R. L. Bradow. Emissions From Trucks by Chassis Version of 1983 Transvent Procedures. SAE Technical Paper No. 801371. 1980.

27. Personal communication with R. Bradow, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 9, 1982.

28. Black,, F. and L. High. Methodology for Determining Particulate and Gaseous Diesel Hydrocarbon Emissions. SAE Technical Paper No. 790422. 1979.

29. Bradow, R. L. Diesel Particulates Emissions. Bull. New York Acad. Med., Vol. 56, No. 9, November-December 1980.

30. Dzubay, T. G., et al. Visibility and Aerosol Composition in Houston, Texas. Environ. Sci. and Tech., 16:(8)514-525, 1982.

31. Chow, J. C., et al. A Neighborhood Scale Study of Inhalable and Fine Suspended Particulate Matter Source Contributions to an Industrial Area in Philadelphia. Paper No. 81-14.1, presented at the 1981 Air Pollution Control Association Annual Meeting, Philadelphia, Pennsylvania.

32. Oldaker, G. B. Condensible Particulate and Its Impact on Particulate Measurements. Entropy Environmentalists, Inc., U.S. EPA Contract No. 68-01-4148, Task No. 69. May 1980.

33. Cooper, J. A., and J. G. Watson. Portland Aerosol Characterization Study. Final Report. Oregon Graduate Center, Beaverton, Oregon. July 31, 1979.

34. Flagan, R., and S. K. Friedlander. Recent Developments in Aerosol Science. D. Shaw (ed.). Wiley-Interscience, New York. 1978.

35. McElroy, M. W., R. C. Carr, D. S. Ensor, and G. R. Markowski. Size Distribution of Fine Particles From Coal Combustion. Science, 215:13-19, 1982.

36. Balfour, W. D., L. P. Edwards, and G. K. Tannahill. Secondary Formation Products in Power Plant Plumes. EPA-600/S7-81-092, 1981.

37. Hegg, D. A., and P. V. Hobbs. Measurements of Gas-to-particle Conversion in the Plumes From Five Coal-fired Electric Power Plants. Atmospheric Environment, 14:99-116, 1980.

38. Whitby, K. T., B. K. Cantrell, and D. B. Kittelson. Nuclei Formation Rates in a Coal-fired Power Plant Plume. Atmospheric Environment, 12: 313-321, 1978.

39. Grosjean, D. Ozone and Other Photochemical Oxidants. National Academy of Sciences. Washington, D. C. 1977.

40. Holt, B. D., R. Kumar, and P. T. Cunningham. Primary Sulfates in Atmospheric Sulfates: Estimation by Oxygen Isotope Ratio Measurements. Science, 217:51-53, 1982.

41. Friedlander, S. K. Recent Developments in Aerosol Science. D. Shaw (ed.). Wiley-Interscience, New York, New York, 1978.

42. Vaeck, L. V., and K. V. Canwenberghe. Cascade Impactor Measurements of the Size Distribution of the Major Classes of Organic Pollutants in Atmospheric Particulate Matter. Atmospheric Environment, 12:2229-2239, 1978.

43. Miguel, A. H., and S. K. Friedlander. Distribution of Benzo(A)Pyrene and Coronene With Respect to Particle Size in Pasadena Aerosols in the Submicron Range. Atmospheric Environment, 12:2407-2413, 1978.

44. Duval, M. M., and S. K. Friedlander. Source Resolution of Polycyclic Aromatic Hydrocarbons in the Los Angeles Atmosphere. Report prepared for U.S. Environmental Protection Agency (Grant No. R806YOY-0251) by the University of California, Los Angeles, California. 1981.

45. Watson, J. G. Receptor Models Relating Ambient Suspended Particulate Matter to Sources. EPA-600/2-81-039, 1981.

46. U.S. Environmental Protection Agency. Protecting Visibility. An EPA Report to Congress. EPA-450/5-79-008, October 1979.

47. U.S. Environmental Protection Agency. Workbook for Estimating Visibility Impairment. EPA-450/4-80-031, November 1980.

48. Dzubay, T. G., et al. Environmental Science and Technology, 16:(2)514-525, 1982.

49. Wolff, et al. The Relationships Between the Chemical Composition of Fine Particles and Visibility in the Detroit Metropolitan Area. Paper No. 82-11M.2, presented at the 1982 Air Pollution Control Association Annual Meeting, New Orleans, Louisiana.

GLOSSARY

Aerosol - Fine solid or liquid matter suspended in gas or air.

Back half - Particulate matter collected in the impingers and all sample-exposed glassware after the filter of either EPA Methods 5 or 17.

Detached plume - Occurrence of a visible plume forming after the exit of a stack with a clear space between the stack and first observance of plume formation.

Filterable particulate - Particulate matter determined by EPA Reference Method 5. For some sources, the amount of "filterable" material collected is a function of the probe and filter temperature.

Fine particulate - Particulate matter with an aerodynamic particle size of usually 2.5 µm or less.

Front half - Particulate matter collected in either EPA Methods 5 or 17 on the filter front half of the probe lines, probe fitting, and probe nozzle.

Inhalable particulate - Respirable particulate matter. The aerodynamic particle size limitation will be defined by EPA upon proposal of the applicable regulation.

PM_{10} - Particulate matter with an aerodynamic particle size of 10 µm (50% cutoff diameter) and less.

Primary particulate - Particulate matter that is formed by the process either prior to or after the control equipment or within the stack or immediately after the stack.

Pseudo particulate/artifact - Particulate matter that would not form in the ambient air but is formed as the result of the conditions and confinement in the sampling train.

Secondary particulate - Particulate matter formed in the ambient air as the result of chemical reactions in the atmosphere.

Soluble organic fraction (SOF) - The portion of the particulate sample extracted by dichloromethane in the mobile source test procedure.

Total particulate - Particulate matter including both the front and back halves of EPA Methods 5 or 17.

APPENDIX A

FORMATION OF CONDENSED PARTICULATE MATTER

For the purposes of this study condensed particulate matter is defined as matter emitted in a gas phase at higher than ambient temperature which then forms particulate matter in the ambient air. As ambient air is entrained, the temperature of the plume drops which causes condensation of some pollutants. The nature of the particulate formed will depend on the source of the emissions. For example, a primary nonferrous smelter emits metallic oxide fumes that condense into inorganic particulate, whereas a textile tenter frame operation emits organic chemicals that condense into organic particulate.

Primary condensed particulate is defined in this study as particulate formed by the physical phenomenon of condensation (or some other mechanism), which is complete before or at a 10:1 dilution ratio in the plume. Gaussian diffusion equations have been applied to determine the distance within which a dilution of 10:1 or greater is achieved. The results indicate that this occurs within 5 meters downwind of the stack. This determination of the plume centerline concentration is based on an assumed windspeed of 1 m/s (the minimum value used in modeling), a stack height of 90 m, and a gas temperature of 436 K. The equations yielded a concentration of less than 2 percent 5 meters downwind of the stack. According to the equation, the desired dilution ratio (10:1) occurred within 1 meter downwind of the stack. Since the equations are not at a limited distance downwind from the source, accuracy of the estimates cannot be assumed as exact. Also, the Gaussian diffusion equations do not consider entrainment and microscale turbulence. Stack parameters such as gas temperature, exit velocity, stack diameter, and stack orifice configuration will have a great effect on the amount of turbulence occurring at the mouth of the stack. All of this leads to a breakdown of the equations within a meter or so of the source. Nevertheless, it is safe to assume the 10:1 dilution ratio occurs within 5 meters downwind of the emission point.

Particles in the atmosphere may be primary or secondary in nature. Primary particulates are those that are emitted in particulate form directly from sources or those that enter the particulate state shortly after their release. Primary particulates are produced directly in the physical or chemical processes peculiar to an emission source. Sources vary; they include those of natural origin, such as volcanoes, forest fires, and wind, as well as those of anthropogenic origin, such as diesel engines, coal combustion, and gravel crushing. Whereas primary particulates may occur in all sizes, secondary particles are usually quite small (<1 μm in diameter).

Secondary particulates are those produced from gases and vapors by chemical and physical processes occurring in the atmosphere after the release of the gases and vapors from their respective sources. Secondary particulates may result from natural events such as the conversion of sulfur dioxide (SO_2) to sulfate formation downwind in an SO_2-laden volcanic plume or from anthropogenic activity such as the gas-to-particle conversion that occurs in smoggy, urban environments.

Both primary and secondary particulates may originate from the same source. For example, coal-fired power plants release large quantities of primary particulate in the form of fly ash. In these same power plants, sulfur impurities in the combustion boiler fuel are oxidized to SO_2, which is subsequently released to the atmosphere and oxidized to secondary particulate (sulfate).

A single compound can act as both primary and secondary particulate matter. Power plant emissions again provide a convenient example. In the boiler, sulfur trioxide (SO_3) and sulfate salts are formed along with SO_2 gas and fly ash. Generally, about 1 percent of the sulfur present in the flue gas exists as SO_3.[4] As the flue gas cools, water vapor can condense and the SO_3-H_2O mixture can form sulfuric acid droplets. These sulfuric acid droplets, along with any sulfate salts present in the plume, are considered primary sulfates; whereas, the sulfates that form downwind as a result of gas-to-particle conversion of the gaseous SO_2 are considered secondary sulfates. Reconciliation of primary and secondary sulfates on the basis of ambient sampling is quite difficult.

Condensed particulate (as defined in this study) is formed in the ambient air by one of three physical mechanisms:

1) Nucleation
2) Condensation
3) Coagulation.

These three mechanisms may form particulate matter, mostly in the submicron range, after the gases exit an air pollution source.

Nucleation

Nucleation is the process in which molecules become physically associated in such a manner as to form a new parcel in a stable liquid phase.[3,4] This process may occur between molecules of the same species or between molecules of different species. The latter process, heteromolecular nucleation, is beyond the scope of the current treatment. Nucleation in the current context is that which occurs between like molecules.

Condensation

Condensation is the physical process in which molecules leave the gas or vapor phase and enter the liquid phase. This process is responsible for most of the gas-to-particle conversion that occurs in the atmosphere. An important parameter controlling condensation is the concentration of the condensing species. Transfer of molecules to the liquid phase occurs only when the vapor concentration exceeds the saturation vapor pressure at existing temperature and pressure conditions. Under supersaturated conditions, condensation will occur to relieve this excess vapor pressure until a saturation ratio of unity is achieved.

Equilibrium thermodynamics provide information on the vapor pressures of particles and droplets and on the conditions at which condensation can occur. The vapor pressure/temperature curves shown in Figure A-1 for two different compounds illustrate factors that could influence the ambient phase distribution of emitted compounds. Based on Figure A-1 it can be determined that:

- The termination of the vapor pressure curve represents the critical point for the substance under consideration. A pure gas at a temperature above its critical temperature cannot be liquified regardless of the degree of compression. Thus, compounds with critical temperatures less than 300 K are always gases at ambient temperatures. In the current effort, such species represent noncondensing species (e.g., He, H_2, Ne, N_2, O_2, NO, CO, CH_4, and C_2H_4).

- A compound having a vapor pressure in excess of the barometric pressure at a given temperature will be in the vapor state and can immediately be classified as volatile. Thus, Compound B will always be in the vapor state at one atmosphere of pressure as long as its temperature exceeds T_1 (Figure A-1). In addition, it is also apparent from Figure A-1 that at atmospheric conditions Compound A is volatile and Compound B is condensable.

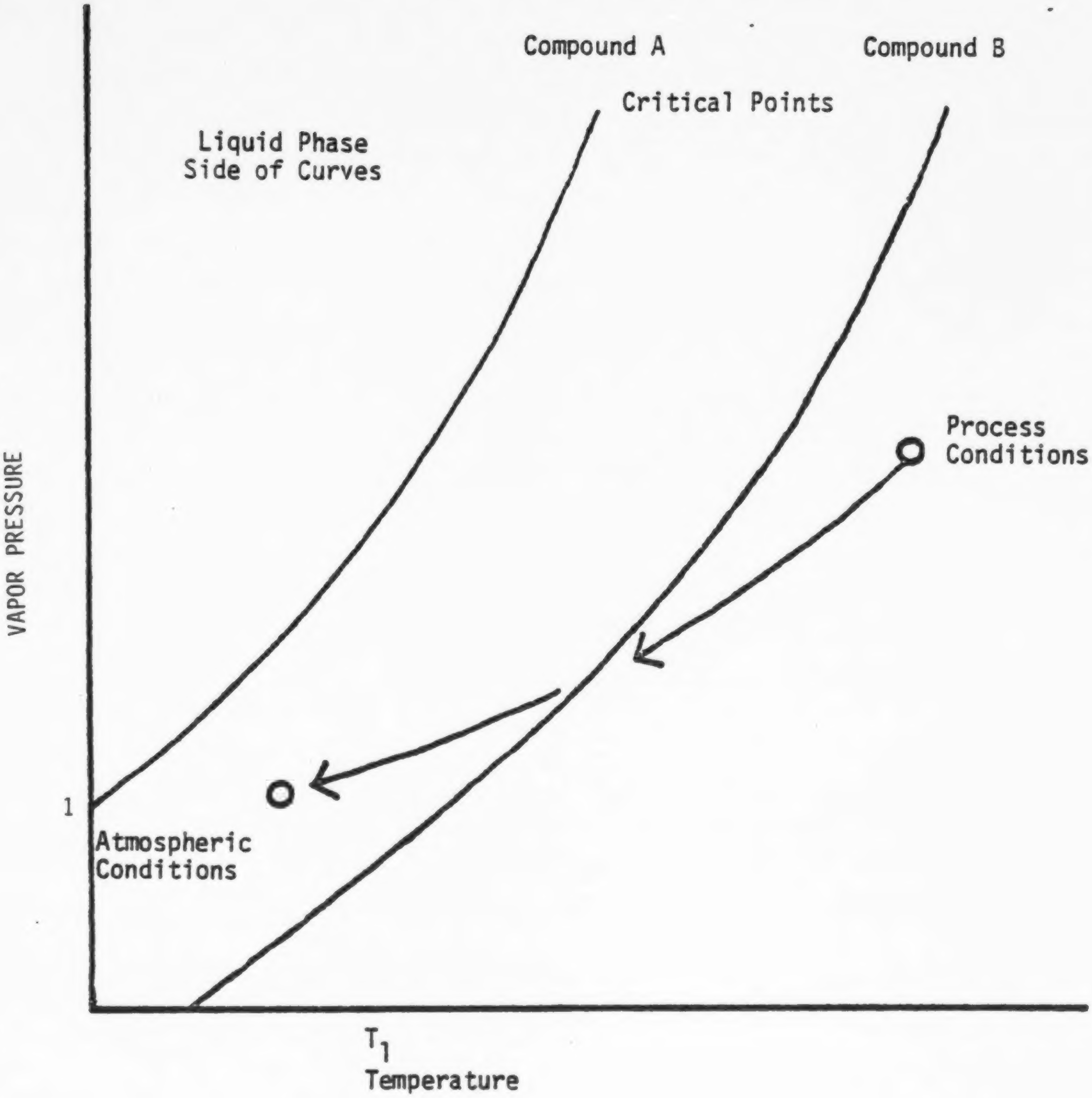


Figure A-1. Vapor pressure curves indicating reversible adiabatic expansion of stack gas from process conditions to atmospheric conditions. Condensation of a compound occurs when its vapor pressure curve is intersected.

- Within an industrial process, the pressure and temperature may be elevated to such a degree that the compound will be in the gaseous state at process conditions, regardless of its phase distribution at ambient conditions. Figure A-1 shows an example of this for Compound B at the point labeled "process conditions." If the compound is emitted into atmospheric conditions via reversible adiabatic expansion or by mixing with cooler air at a lower concentration, a portion of the compound will condense into a fine aerosol. This occurs when the gas-phase concentration of the species exceeds its gas phase saturation concentration.

The distribution of components between phases is governed by thermodynamic equilibrium.[3,4] Supersaturation of a vapor mixture produced by cooling or chemical reaction is relieved by formation of a liquid phase. Condensation usually takes place on the curved surface of a droplet. As the droplet diameter becomes smaller than 1 μm, fewer molecules are adjacent to the surface than for a flat surface. This permits liquid molecules on the surface of the droplet to escape more easily, which increases the vapor pressure over a droplet with decreasing droplet diameter. This is known as the Kelvin effect and is described by Equation (1):

$$\frac{P_d}{P_o} = \exp\left[\frac{4\sigma\nu}{dkT}\right] \qquad \text{Equation (1)}$$

where

P_d = the equilibrium vapor pressure over particle diameter d
P_o = the partial pressure at a flat surface
σ = the surface tension
ν = the molecular volume
k = Boltzman's constant.

The Kelvin effect suggests that condensation will not occur on small particles unless the vapor pressure of the condensing species substantially exceeds the saturation vapor pressure.[5] Condensation becomes "easier" with increasing particle diameter, as the importance of the Kelvin effect diminishes. Thus, the Kelvin effect sets a lower limit on the particle size of a polydisperse aerosol that can serve as condensation nuclei.

In contrast, the presence of a nonvolatile solute in a solvent solution tends to reduce the vapor pressure of the solvent to an extent dependent upon the nature and concentration of the solute. Thus, because vapor pressure lowers as a result of the presence of a solute, a solution droplet can grow via condensation in an atmosphere that is not saturated in either component.

Expressions describing the rate at which condensation occurs (F) depend to a large extent on the particle size under consideration and are presented in Table A-1.[3,4] When the Kelvin effect is important, the partial pressure driving force in the expressions in the table must be corrected to account for the increased equilibrium vapor pressure resulting from particle curvature.

As discussed above, gas-to-particle conversion can occur by both nucleation and condensation. In addition, chemical reactions occurring within the droplet or upon the surface of the particle can also result in gas-to-particle conversion. Growth laws are expressions for the change in particle volume or particle diameter with time. Growth laws for condensation and for chemical reaction are presented in Table A-2.[6] Comparison of measured results with these theoretical expressions can be used to gain insight on the gas-to-particle conversion mechanism that occurs. By matching data with growth laws it is possible to identify mechanisms that are consistent with data and to exclude those that are inconsistent. This approach has been used by McMurry and Wilson (1982)[6] to suggest that droplet phase reactions were important in accounting for growth of aerosols measured under humid ambient conditions in the Great Smokey Mountains, because condensation was an important growth mechanism in low-humidity smog-chamber experiments.

Nucleation generates high concentrations of very small particles, whereas the number of particles is a factor in the growth of particles by condensation. Criteria for determining which process controls gas-to-particle conversion have been developed by Friedlander (1977)[3] and McMurry and Friedlander (1979).[7] These criteria are complex and beyond the scope of this study. Husar and Whitby (1973)[8] have presented data that suggest nucleation may be important for aerosol surface area concentrations below 500 $\mu m^2/cm^3$, however, condensation may be important above this value. For most sources it is likely that pre-existing aerosol in the stack and near stack plume will be sufficient to promote condensation as the primary gas-to-particle mechanism.

TABLE A-1. RATE EXPRESSIONS FOR CONDENSATION[a]

Particle size, µm	Knudsen number	Regime	Rate expression	Equation
$d >> 0.1$	$Kn << 1$	Continuum	$F = \frac{2\pi Dd}{kT} (P_1 - P_d)$	(2)
$d \sim 0.1$	$Kn \sim 1$	Transition	$F = 2\pi Dd(n_1 - n_d) \quad \frac{1+Kn}{1+1.71Kn+1.333Kn^2}$	(3)
$d << 0.1$	$Kn >> 1$	Free molecule	$F = \frac{d^2 P_1 (P_1 - P_d)}{2mkT}$	(4)

[a] In these expressions, D is the gaseous diffusitivity; n_d is the concentration and P_d is the partial pressure in equilibrium with the surface; n_1 is the bulk concentration and P_1 is the bulk partial pressure; and Kn is Knudsen number (Kn = 2 liters/d = ratio of the mean free path of the condensing species to the particle radius.

TABLE A-2. THEORETICAL GROWTH LAWS

Mechanism controlled by	Volume growth rate	Diameter growth rate
Condensation		
Continuum	$\alpha\ d$	$\alpha\ d^{-1}$
Transition	$\alpha\ d$, $f(Kn)$	$\alpha\ d^{-1} f(Kn)$
Free molecule	$\alpha\ d^2$	$\alpha\ d^0$
Surface reaction	$\alpha\ d^2$	$\alpha\ d^0$
Volume reaction	$\alpha\ d^3$	$\alpha\ d$

Coagulation

Coagulation is the process in which particles come into contact with one another and coalesce.[3,9] Because coagulation is a mass-conserving process, it only acts on an aerosol system to modify its size distribution. Coagulation is governed by the Brownian motion of particles and by their interaction at very short distances. The rate of coagulation is approximated by the number of particle collisions per unit time per volume. For an initially monodisperse aerosol system, the number of particles per unit volume, N, is diminished by coagulation at a rate described by Equation (5):

$$\frac{dN}{dt} = \frac{-K_o\ N^2}{2} \qquad \text{Equation (5)}$$

The coagulation constant, K_o, is equivalent to $8\pi dD$ or $8kT/3\mu$ or 6×10^{-10} cm^3/s,

where

D = particle diffusivity
μ = the gas viscosity.

In this system, the initial diameter will be the minimum, and over time coagulation will increase both the mode and the breadth of the size distribution. This does not continue indefinitely, because for a polydisperse system, the highest rate of coagulation on a per-particle basis occurs on particles at opposite ends of the size distribution. The smallest particles combine with the largest at a faster rate than with any other size. The addition of a small particle does not significantly alter the size of the large particle. The apparent effect of coagulation on an aerosol system is the removal of small particles from the distribution with no overall change in mass. Coagulation can therefore be thought of qualitatively as acting to establish and maintain a particle size distribution of moderate breadth.

CHEMICAL COMPOSITION OF CONDENSED PARTICULATE MATTER

Very little direct data were found on the chemical composition of condensed particulate matter; however, based on the chemical and physical properties of organic and inorganic compounds, certain hypotheses indicate that certain classes of compounds will form condensed particulate.

Organic Compounds

Generally speaking, any organic compound that is emitted from an air pollution source to the atmosphere in the vapor state and is normally a solid at ambient temperatures will condense once the critical temperature and pressure are reached for a given compound. This condensation is a physical phenomenon.[10] In tests conducted on mobile sources, it was found that condensation occurred most readily with C_{15} and greater organic species.[11]

Higher-molecular-weight organic compounds such as polycyclic organic matter (POM) have been collected from stationary sources with a modified EPA Method 5 sampling train. Part of the collected POM passed through the filter portion of the train and was trapped by condensation, however, the exact portion was not reported.[12]

Inorganic Compounds

The behavior of inorganic compounds with respect to condensation appears to be less predictable than that of organic compounds because of the flue gas temperatures or the reactions taking place with the species present in many stationary source stack gas effluent streams.

Vaporous species of inorganic compounds such as SiO_2, MgO, heavy metal oxides, Na_2SO_4, K_2SO_4, NaCl, and PbO have been found in the flue gas from coal combustion.[13] Compounds such as SiO_2, Na_2SO_4, and K_2SO_4 generally condense in the stack, but other species such as PbO may remain in the vapor state.[13] It has been suggested that some of the materials with higher condensation temperatures, such as SiO_2, might be condensing on the surface of other particles as they leave the combustion zone, but before they exit to the atmosphere. Therefore, whether they formed homogeneous or heterogeneous condensation products, the metallic oxides would generally follow thermodynamic predictions for condensation when the condensation temperatures were above 1300 K.[13]

At sources such as primary nonferrous smelters and large fossil fuel-fired combustion units, some inorganic species do have significant vapor pressure at typical stack temperatures. Typical metallic oxides found in the flue gas of coal combustion sources are metals such as As, Mn, Ni, Pb, V, and Se, and in lesser amounts, Cd.[14] At elevated temperatures, most of these species have a vapor pressure that allows some of the material to remain gaseous. This material will subsequently condense when the temperature approaches ambient conditions. Arsenic trioxide, for example, has a high vapor pressure ($100^{o}C$) relative to other metal oxides.[15] This high vapor pressure means that at least some of the arsenic trioxide will escape as a vapor. At $100^{o}C$, one estimate of arsenic trioxide vapor concentration in a gas stream is 4.30×10^{-3} g/m^3.[15]

Sulfate compounds make up the largest category of inorganic condensable emissions. Sulfates are formed as the result of the sulfur content of either the raw material being processed or the fuel being burned. The sulfur is converted to SO_2 and SO_3 by oxidation, and it reacts with other compounds or elements, either in the combustion or process zone or in the stack gases. As discussed earlier, sulfates formed some distance from the source are considered secondary particulate and are not included in this study.

Sulfuric acid mist is a condensed particulate (for the purposes of this study) formed in flue gases of combustion sources. The reactants, SO_3 and H_2O, are present in flue gas from sources that burn fuel containing sulfur. Sulfuric acid is not a filterable material, and a modified EPA Method 6 is required to test for sulfuric acid emissions from combustion sources.[16]

Ammonia plays a very significant role in the production of sulfates. This common gas is generated primarily as a result of soil bacteria decomposing amino acids in the natural environment. Estimates of the amount of natural ammonia generated yearly range from 1169 to 5900 million tons. Industrial sources, primarily fossil fuel combustion, contribute about 4 million tons/year. The residence time for ammonia has been estimated to be about 7 days, and it is the primary source of gaseous alkaline emissions. It serves to neutralize acidic compounds such as sulfur dioxide and nitrogen dioxide.[17]

Evidence suggests that ammonia reacts with sulfur oxides and forms ammonium sulfoxide compounds. Whitby (1978),[18] Friend (1974),[19] Roesler (1965),[20] Kircher (1977),[21] and Husar (1978)[22] report evidence that many of these ammonium sulfoxide compounds exist as ammonium sulfate. Eatough (1978)[23] suggests that a considerable fraction of the observed ambient aerosol sulfoxides may be inorganic sulfites, which are relatively stable. These sulfites appear to be oxidized to sulfate very slowly, with half-lives measured in years.

Some possible ammonium sulfoxide compounds that are stable at ambient temperatures include ammonium sulfate ($(NH_4)_2SO_4$), ammonium bisulfate (NH_4HSO_4), ammonium sulfite ($(NH_4)_2SO_3 \cdot H_2O$), ammonium bisulfite (NH_4HSO_3), sulfamic acid (NH_3SO_3), ammonium sulfamate ($NH_4SO_3NH_2$), ammonium dithionate ($(NH_4)_2S_2O_6$), and ammonium persulfate ($(NH_4)_2S_2O_8$). Combinations of these salts, with substituted cations forming complex salts, are also possible. The stability of such compounds, as indicated by the ammonia vapor pressure that they exert, is apparently very sensitive to trace contaminants and acidic impurities (see Scott 1979).[24] Pure ammonium sulfate, however, is a stable solid at temperatures up to 950°F. Pure ammonium bisulfate boils at about 900°F.[17]

The oxidation of sulfur dioxide in aqueous systems is very sensitive to catalysis and pH.[25] Ammonia is believed to be one of the most effective agents for promoting these reactions. One of the first reported studies of ammonia-catalyzed SO_2 oxidation in water droplets was conducted by van den Heuvel (1963).[26] The researchers observed extremely rapid oxidation, on the order of 10 percent per minute, under laboratory conditions. Much slower, but very significant rates for natural systems, have been described by McKay (1971)[27] and Adamowicz (1979).[28] The presence of ammonia and sulfur dioxide in water droplets results in rapid oxidation and formation of ammonium sulfoxide compounds. Relatively high concentrations of ammonia are expected to promote very rapid formation of aerosol particles; however, these rapid reactions take place only if an aqueous phase is present. Gas phase reactions between ammonia and sulfur dioxide proceed much more slowly. In the natural environment, formation of fog, rain, or other precipitation is expected to enhance significantly the reactions between natural ammonia sources and sulfur dioxide.[17]

The absorption of sulfur dioxide in water has been studied in detail by Carmichael and Peters (1979).[29] The chemical reactions of sulfur dioxide in aqueous solutions presented in this report apply to rain drops, surface water bodies, or stack sampling impingers. They present an equilibrium distribution of sulfur species in the plus-four oxidation state S(IV) as illustrated in Figure A-2. Dilute sulfur dioxide going into solution exists primarily as bisulfite ions. The initial pH of a raindrop in a sulfur dioxide atmosphere is about six. The pH changes rapidly to between 4 to 5 as more

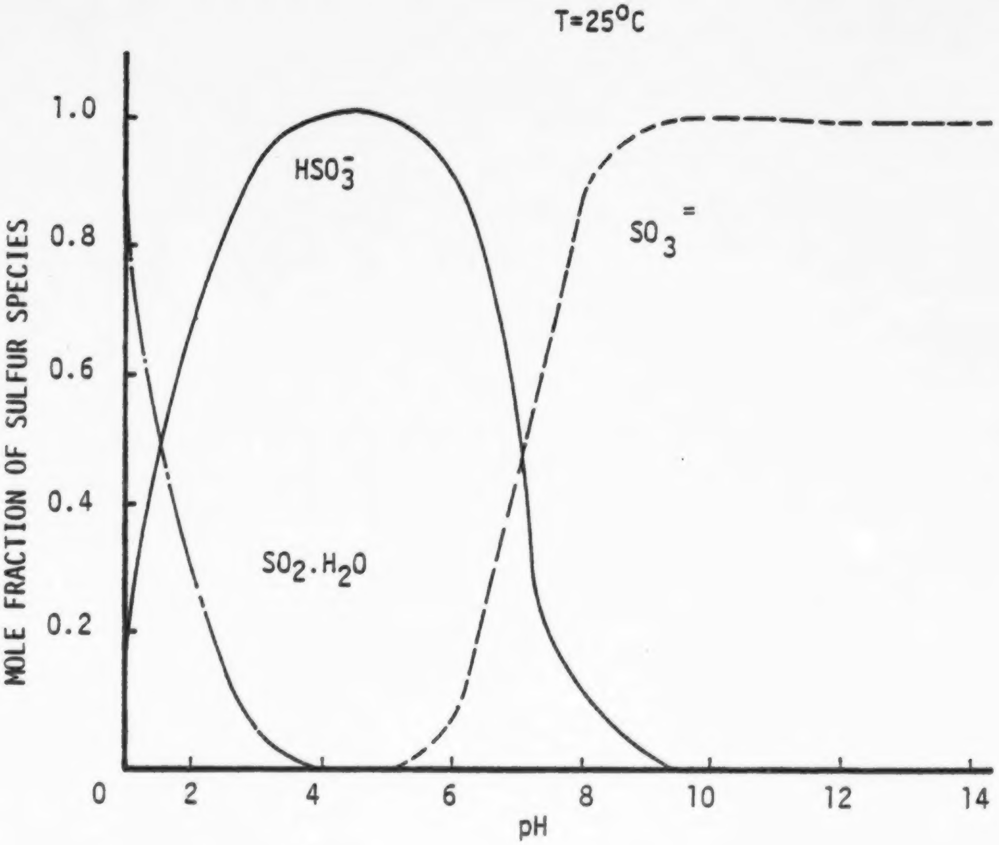


Figure A-2. Distribution of S(IV) species concentrations as a function of solution pH.[29]

sulfur dioxide enters the system. The reduced pH drives the equilibrium toward the $SO_2 \cdot H_2O$ species.

Since the presence of ammonia promotes $SO_3^=$ formation in an aqueous system (that readily oxidizes to $SO_4^=$), it may be one of the primary factors in the formation of condensable sulfate particulate. It also chemically combines with the $SO_4^=$ to form particulate such as NH_4HSO_4 and $(NH_4)_2SO_4$, common sulfate species.

REFERENCES

1. U.S. Environmental Protection Agency. User's Guide for MPTER. EPA-600/8-80-016, April 1980.

2. User's Guide for PTPLU. Aerocomp, Inc. U.S. EPA Contract No. 68-02-3442. May 1982.

3. Friedlander, S. K. Smoke, Dust, and Haze. Wiley-Interscience, New York. 1977.

4. Friedlander, S. K. Recent Developments in Aerosol Science. D. Shaw (ed.) Wiley-Interscience, New York. 1978.

5. Green, H. L., and W. R. Lane. Particulate Clouds: Dusts, Smokes and Mists. E and F. N. Spon Ltd., London. 1964.

6. McMurry, P. H., and J. C. Wilson. Growth Laws for the Formation of Secondary Ambient Aerosols: Implications for Chemical Conversion Mechanisms. Atmospheric Environment, 16:121-134, 1982.

7. McMurry, P. H., and S. K. Friedlander. New Particle Formation in the Presence of an Aerosol. Atmospheric Environment, 13:1635-1651, 1979.

8. Whitby, K. T., R. B. Husar, and B. Y. Liu. The Aerosol Size Distribution of Los Angeles Smog. Journal of Colloid and Interface Science, 39:177-204, 1972.

9. Smoluchowsky, M. V. Mathematical Theory of the Kinetics of the Coagulation of Colloidal Solutions. Z Phys Chem, 92:129-137, 1917.

10. Metcalfe, H. C., J. E. Williams, and J. F. Castka. Modern Chemistry, Holt, Rinehart, and Winston, Inc. 1966.

11. Personal communication from R. Bradow, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 9, 1982.

12. U.S. Environmental Protection Agency. Preliminary Assessment of the Sources, Control and Population Exposure to Airborne Polycyclic Organic Matter (POM) as Indicated by Benzo(a)Pyrene (BaP). Final Report. November 10, 1978.

13. McWallan, J. J., G. J. Yurek, and J. F. Elliot. Combustion and Flame. Volume 42:45-60. 1981.

14. Radian Corporation. Trace Metals and Conventional Combustion Sources. U.S. EPA Contract No. 68-02-2608. April 1980.

15. Hellwig, G. V., and T. Mappes. Extended Source Survey Report for Arsenic. PEDCo Environmental, Inc. U.S. EPA Contract No. 68-02-3173, Task No. 34. May 1982.

16. Cheney, J. L., and J. T. Chehaske. Measurement of Primary Sulfates with an Acid Condensation System. Paper No. 82-58.9, presented at the 1982 Air Pollution Control Association Annual Meeting.

17. Chadbourne, J. F., et al. Reactive Plumes - Sampling and Opacity Concerns for Cement Kilns. Paper No. 80-12.4, presented at the 1980 Air Pollution Control Association Annual Meeting, Montreal, Canada.

18. Whitby, K. T., et al. Nuclei Formation Rates in a Coal-Fired Power Plant Plume. Atmospheric Environment, 12:313-321, 1978.

19. Friend, J. P. Formation of Atmospheric Aerosols by Gas to Particle Conversions. AICHE Symposium, Sat., 701:267-220. 1974.

20. Raesler, J. F., H. J. R. Stevenson, and J. S. Nader. Size Distribution of Sulfate Aerosols in Ambient Air. Journal of Air Pollution Control Association, 15:576-579. 1965.

21. Kircher, J. F., et al. A Survey of Sulfate, Nitrate, and Acid Aerosol Emissions and Their Control. EPA-600/7-77-04. NTIS PB-267 588.

22. Husar, R. B., J. P. Lodge Jr., and D. J. Moore. Sulfur in the Atmosphere. Atmospheric Environment, 12:7-23, 1978.

23. Eatough, D. J., et al. The Formation and Stability of Aerosol Sulfate Species in Aerosols. Atmospheric Environment, 12:263-271, 1982.

24. Scott, W. D., and F. C. R. Cattell. Vapor Pressure of Ammonium Sulfates. Atmospheric Environment, 13:307-317, 1979.

25. Fuller, E. C., and R. H. Gist. The Rate of Oxidation of Sulfite Ions by Oxygen. J. Am. Chem. Soc. 63:1644-1650, 1941.

26. Van den Heuvel, A. P., and B. J. Mason. The Formation of Ammonium Sulfate in Water Droplets Exposed to Gaseous Sulfur Dioxide and Ammonia. Quart J. Roy. Meteorol. soc., 89:271-275, 1963.

27. McKay, H. A. C. The Atmospheric Oxidation of Sulfur Dioxide in Water Droplets in the Presence of Ammonia. Atmospheric Environment, 5:7-14, 1971.

28. Adamowicz, R. F. A Model for the Reversible Washout of Sulfur Dioxide, Ammonium and Carbon Dioxide From a Polluted Atmosphere and the Production of Sulfates in Raindrops. Atmospheric Environment, 13:105-121, 1979.

29. Carmichael, G. R., and L. K. Peters. Some Aspects of SO_2 Absorption by Water - Generalized Treatment. Atmospheric Enviornment, 13:1505-1513, 1979.

APPENDIX B

FILTERABLE VS. CONDENSED PARTICULATE MATTER AND ADJUSTED EMISSION FACTORS

EPA METHOD 5 TEST RESULTS--RATIO OF FILTERABLES TO BACK HALF CATCH, BY SOURCE CATEGORY[a]

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Anode baking furnace	97.32	2.68		
	58.46	41.54		
	98.63	1.37		
	74.94	25.06		
	33.66	66.33		
	47.80	52.19		
	49.53	50.47		
			34.2	23.4
Asphalt plants	75.7	24.3		
	68.6	31.4		
	32.5	67.5		
	21.5	78.5		
	48.8	51.2		
	20.6	79.4		
	85.3	14.7		
	20.6	79.4		
	86.1	13.9		
	95.0	5.0		
	92.3	7.7		
	97.6	12.4		
	88.6	10.9		
	97.3	2.6		
	87.5	12.5		
			32.8	29.3
Boiler/coal (industrial)	97.14	2.86		
	88.91	11.09		
	88.45	11.55		
	88.35	11.65		
	96.91	3.09		
	88.60	11.40		
	81.22	18.78		
	90.97	9.03		
	98.70	1.30		
	81.50	18.50		
			9.9	5.77

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Boiler/coal (utility)	16.07	83.93		
	0.71	99.29		
	80.00	20.00		
	83.72	16.28		
	83.33	16.67		
	51.09	48.91		
	94.52	5.49		
	86.11	13.89		
	58.07	41.93		
	97.57	2.43		
	7.33	92.67		
	27.25	72.75		
	23.40	77.60		
	76.70	23.50		
	50.80	49.20		
			44.3	33.44
Boiler/oil	61.38	38.62		
	64.65	35.35		
	68.82	31.18		
	63.75	36.25		
	44.95	55.05		
	75.69	24.31		
	60.07	39.93		
	16.03	83.97		
	31.78	68.22		
	32.46	67.54		
	50.53	49.47		
	45.20	54.80		
	56.97	33.02		
	14.70	85.30		
	22.40	76.60		
	20.43	79.57		
	49.05	50.95		
	25.31	74.69		
	25.77	74.23		
	24.34	75.66		
	46.89	53.11		
	35.67	56.41		
	41.27	30.69		
	26.59	73.41		
	36.05	63.95		
	19.19	80.18		
	45.38	54.62		
			57.3	18.38

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Boiler/wood	25.82	74.18		
	85.02	14.98		
	91.72	8.28		
	100.00	0.00		
	100.00	0.00		
	82.80	17.20		
	66.60	33.40		
	89.90	10.10		
	92.00	8.00		
	88.90	10.10		
	80.80	19.20		
	79.20	20.80		
	96.80	3.20		
	94.90	5.10		
			16.0	18.34
Brick and tile plant kilns	92.57	7.43		
	99.54	0.46		
	95.45	4.55		
	91.86	8.14		
	64.78	35.22		
	82.36	17.64		
	36.38	63.62		
	31.18	68.82		
	55.85	44.15		
			27.8	24.70
Chemical production				
Potassium still	65.32	34.68		
Chrome oxide kiln	94.31	5.61		
Boric acid	16.17	83.83		
Boric acid	70.94	29.06		
			38.3	
Elemental phosphorous	46.0	54.0		
Fiberboard dryer	95.59	4.41		
	19.36	80.64		
			42.5	38.1

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Glass plants	8.85	91.15		
	85.53	14.47		
	83.72	16.28		
	85.31	14.69		
	74.62	25.38		
	53.52	46.48		
	56.10	43.90		
	90.00	10.00		
	92.70	7.30		
	94.20	5.80		
	85.60	14.40		
	63.80	36.20		
	67.10	32.90		
	80.40	19.60		
			27.0	21.8
Grain dryers	74.29	25.71		
	95.43	4.56		
	53.88	46.12		
			25.5	17.0
Incinerators				
Municipal	4.17	95.83		
	93.55	6.45		
	85.00	15.00		
	96.20	3.80		
			30.3	38.10
Industrial	35.26	64.74		
Sewage sludge	79.14	20.86		
	44.40	55.60		
			38.2	17.40
Iron foundries	93.47	6.53		
	90.20	9.80		
	65.20	33.80		
	65.10	34.90		
	49.90	50.10		
	93.50	6.50		
			23.6	16.9

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Iron and steel sinter plant	9.55	90.45		
	88.43	11.57		
	79.80	20.20		
	85.50	14.50		
	92.50	7.50		
	57.80	42.20		
	63.40	36.50		
	86.80	13.20		
	99.70	0.30		
	57.70	42.30		
	66.80	33.20		
	45.30	54.70		
	81.50	18.40		
	76.40	23.60		
			29.2	22.6
Electric arc furnaces	59.38	40.62		
	51.90	48.10		
	97.79	2.21		
	98.13	1.87		
	97.47	2.52		
	97.99	2.01		
			16.2	20.8
Basic oxygen furnace	66.5	33.5		
	30.0	70.0		
	92.3	7.7		
			37.1	25.6
Open hearth	55.51	44.49		
	90.41	9.59		
	49.72	14.04		
			22.7	15.5
Coke ovens	43.10	56.90		
	68.75	31.25		
	91.53	8.47		
	83.40	16.60		
			28.3	18.4

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Sand blast (steel)	36.96	63.04		
	99.67	0.32		
Heat treat (steel)	45.47	54.53		
	93.23	6.77		
Kraft pulp and paper mills				
Recovery boilers	99.55	4.45		
	97.14	2.86		
	76.80	23.20		
	89.00	11.00		
	92.50	7.50		
	93.80	6.20		
	45.70	54.30		
	92.10	7.90		
	89.50	10.50		
	85.20	14.80		
			14.3	14.4
Lime kiln	72.00	28.00		
	94.80	5.20		
	54.50	45.50		
	75.10	24.90		
	31.60	68.40		
	37.30	62.70		
			39.1	22.1
Smelt dissolve tank	66.60	33.40		
	62.70	37.30		
	97.40	2.50		
	89.60	10.50		
	93.00	7.00		
	93.70	6.30		
			16.2	13.8
Lime kiln	94.97	5.03		
	79.64	20.36		
	94.20	5.80		
			10.4	7.1

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Mineral products				
Gypsum	87.28	12.72		
Clay dryer	0.49	99.51		
Feldspar dryer	11.60	88.40		
Clay products kiln	80.80	19.20		
	94.10	5.90		
			12.6	6.6
Mineral wool	45.40	54.60		
	99.16	1.64		
	38.37	61.63		
			39.3	26.80
Petroleum refineries				
Heaters	45.6	54.4		
FCC	97.6	2.6		
	54.8	45.2		
			23.9	21.3
Catalytic regenerator	43.2	56.8		
	69.9	30.1		
	26.6	73.4		
			53.4	17.8
Portland cement				
Kiln (gas-fired)	90.08	9.92		
Kiln (coal-fired)	73.84	26.16		
Kiln (wet-process)	69.0	31.0		
	58.5	41.5		
	47.7	52.3		
	48.0	52.0		
	53.2	46.8		
	58.7	41.3		
	96.1	3.9		
	92.6	7.4		
			34.5	17.9

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Kiln (dry process)	37.90	62.10		
Kiln (process not specified)	46.43	53.57		
	81.10	18.90		
	82.90	17.10		
	48.00	52.00		
			35.4	
Finish mill (wet-process)	66.5	33.5		
	63.2	36.8		
	91.0	9.0		
			26.4	12.4
Primary nonferrous smelters				
Zinc sweat kiln	24.73	75.27		
Zinc fume kiln	86.57	13.43		
Zinc ore briquet dryer	82.68	17.32		
Lead sinter line	99.9	0.1		
	91.3	8.7		
			4.4	4.3
Lead blast furnace	37.7	62.3		
Copper converter	69.5	30.5		
Copper converter, electric furnace, and fluid bed roaster	39.77	60.23		
Copper reverberatory furnace	44.50	55.50		
Copper roasters	99.00	1.00		
Molybdenum roasters	97.04	2.96		
Roofing				
Saturated felt	65.6	34.4		
	45.8	54.2		
			44.3	9.9

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Asphalt blowing	14.62	85.38		
	12.71	87.27		
	100.00	0.00		
	100.00	0.00		
			43.2	43.2
Secondary metal smelters				
Aluminum dross furnace	11.11	88.89		
Aluminum furnace	33.73	66.26		
Lead furnace	88.58	11.42		
	71.70	18.30		
	23.50	76.50		
	27.80	72.20		
	18.70	81.30		
	5.80	94.20		
	63.00	37.00		
			55.8	30.6
PbO_2 mills	47.19	52.81		
Lead grid casting	34.90	65.10		
	42.95	57.05		
	54.48	45.52		
	81.74	18.26		
			47.7	16.0
Lead remelt pot	89.83	10.17		
Nonferrous metal reclamation furnace	85.00	15.00		
	11.90	88.10		
	96.60	3.40		
			35.5	37.5
Silicone carbide furnaces (Acheson furnace)	17.80	82.20		
	89.12	10.88		
	83.82	16.18		
	82.40	17.60		
			31.7	29.2

(continued)

EPA Method 5 Test Results (continued)

Category/subcategory	Filterables, %	Back half, %	Back half, mean, %	Back half, σ, %
Spray paint booths	46.09	53.91		
	63.49	36.51		
	72.23	27.77		
	66.90	33.10		
			37.8	9.8
Textile				
Dryers	24.65	75.34		
Tenter frame	9.1	90.1		
	18.5	81.5		
	4.2	95.8		
	23.9	76.1		
			85.9	7.6
Wood products				
Sanding	26.62	73.38		
	94.04	5.96		
	99.41	0.59		
			26.6	40.6
Resawing	83.65	16.35		
	99.69	0.31		
			8.3	8.0

[a] Test results reflect emissions after air pollution control equipment.

ADJUSTED EMISSION FACTORS
[g/Mg (lb/ton)]

Source category	Unadjusted emission factor[a,b]	Emission factor adjusted for condensables	Quantity attributable to condensable in IP range[a]
Anode baking furnace			
Uncontrolled	1.5 (3.0)	2.3 (4.6)	0.8 (1.6)
Asphalt plants			
Venturi scrubber	0.15 (0.3)	0.2 (0.4)	0.05 (0.1)
Baghouse	0.05 (0.1)	0.07 (0.13)	0.02 (0.03)
Boiler - coal			
Industrial			
Uncontrolled	6.5 (13A)	6.6A (13.2A)	0.1A (0.2A)
Utility			
Uncontrolled	8A (16A)	8.4A (16.8A)	0.4A (0.8A)
Boiler - oil			
Utility			
kg/10^3 liters (lb/10^3 gal)	1 (8)	2.3 (18.7)	1.3 (10.7)
Industrial			
kg/10^3 liters (lb/10^3 gal)	2.75 (23)	6.45 (54)	3.7 (31)
Boiler - wood	2.5-7.5 (5-15)	3.0-8.9 (6.0-17.8)	0.5-1.4(1.0-2.8)
Brick and tile plants			
Oil	0.3 (0.6)	0.4 (0.8)	0.1 (0.2)
Coal	0.5A (1A)	0.7A (1.4A)	0.2A (0.4A)
Chemical production	N/A		
Elemental phosphorus	N/A		
Fiberboard	0.3 (0.6)	0.5 (1.0)	0.2 (0.4)
Glass plants	1 (2)	1.4 (2.8)	0.4 (0.8)
Grain dryers	3 (6)	4.0 (8.0)	1.0 (2.0)
(continued)			

Adjusted Emission Factors (continued)

Source category	Unadjusted emission factor[a,b]	Emission factor adjusted for condensables	Quantity attributable to condensable in IP range[a]
Incinerators			
Municipal			
Uncontrolled	15 (30)	15.5 (30)	0.5 (1.0)
Industrial			
Uncontrolled	3.5 (7.0)	3.7 (7.4)	0.2 (0.4)
Sewage sludge			
Uncontrolled	50 (100)	52 (104)	2 (4)
Iron foundries			
Uncontrolled	8.5 (17)	8.7 (17.4)	0.2 (0.4)
Iron and steel			
Sinterplant			
Uncontrolled	10 (20)	10.3 (20.6)	0.3 (0.6)
Electric arc furnace			
Uncontrolled	3.5-5.3(7.0-10.6)	3.6-5.4(7.2-10.8)	0.1 (0.2)
BOF			
Uncontrolled	16-43 (32-86)	16.7-44.8(33.4-89.6)	0.7-1.8(1.4-3.6)
Open hearth			
Uncontrolled	2.9-6.0(5.8-12.0)	3.0-6.1(6.0-12.2)	0.1 (0.2)
Coke ovens coking cycle	0.05 (0.1)	0.07 (0.14)	0.02 (0.04)
Kraft pulp & paper			
Recovery boilers			
Untreated and uncontrolled	75 (150)	76.1 (152.2)	1.1 (2.2)
Lime kiln			
Uncontrolled	22.5 (45)	23.4 (46.8)	0.9 (1.8)
Smelt dissolve tank			
Uncontrolled	2.5 (5)	3.0 (6)	0.5 (1)
Lime kiln			
Uncontrolled	100 (200)	101 (202)	1 (2)

(continued)

Adjusted Emission Factors (continued)

Source category	Unadjusted emission factor[a,b]	Emission factor adjusted for condensables	Quantity attributable to condensable in IP range[a]
Mineral Products			
Gypsum			
Uncontrolled	45 (90)	45.6 (91.2)	0.6 (1.2)
Clay dryer			
Uncontrolled	35 (70)	38.9 (77.8)	3.9 (7.8)
Mineral wool cupola	11 (22)	18 (49)	7 (27)
Petroleum refining			
Heaters kg/10^3 liters (lb/10^3 bbl) of oil burned)	2.4 (840)	4.0 (1384)	1.6 (544)
FCC (uncontrolled) kg/10^3 liters (lb/10^3 bbl) of fresh feed)	0.695(242)	0.913 (318)	0.218 (76)
Portland cement			
Kiln (wet-process)	114 (228)	174 (348)	60 (120)
Kiln (dry-process)	122 (245)	323 (646)	201 (402)
Primary nonferrous smelters			
Pb sinterline			
Downdraft, uncontrolled	106.5(213.0)	106.9 (213.8)	0.4 (0.8)
Lead blast furnace	180.5(361.0)	478 (957)	298 (596)
Copper converter	30 (60)	43 (86)	13 (26)
Copper roaster	22.5 (45)	22.7 (45.4)	0.2 (0.4)
Roofing			
Saturated felt	1 (2)	1.4 (2.8)	0.4 (0.8)
Blowing	1.25 (2.5)	2.24 (4.48)	0.99 (1.98)

(continued)

Adjusted Emission Factors (continued)

Source category	Unadjusted emission factor[a,b]	Emission factor adjusted for condensables	Quantity attributable to condensable in IP range[a]
Secondary metal smelters			
Aluminum dross furnace			
Uncontrolled	7.25 (14.5)	8.0 (16.0)	13.2 (26.4)
Controlled	1.65 (3.3)	14.85 (29.7)	13.2 (26.4)
Aluminum furnace			
Reverberatory			
Uncontrolled	2.15 (4.3)	2.29 (4.58)	1.28 (2.56)
Controlled	0.65 (1.3)	1.08 (2.16)	1.28 (2.56)
Lead furnace			
Uncontrolled	96.5 (193)	100.5 (201.0)	4.0 (8.0)
Lead remelt pot			
Uncontrolled	0.4 (0.8)	0.90 (1.8)	0.5 (1.0)

[a] A = percent ash.

[b] N/A = not available.

APPENDIX C

DISCUSSIONS OF EPA METHODS 5 AND 17, MODIFIED METHOD 5, AND THE STACK DILUTION SAMPLING SYSTEM

The following paragraphs discuss standard particulate testing methods and their relationship to measuring primary particulates. The discussions are arranged in order of increasing capability for measuring primary particulate matter. For each method the following points are emphasized: a) the purpose associated with the method's use and what the method is intended to quantify; b) the component parts of the method's sampling train that figure prominently in the actual collection of particulate matter (e.g., probes, filters, and impingers); and c) the method's limitations from the standpoint of artifact formation and other biases.

EPA REFERENCE METHOD 17

Reference Method 17[1] is the most commonly applied of a group of similar methods, all of which entail an in situ filtration technique for the determination of particulate matter mass concentrations. [The other methods are the American Society for Mechanical Engineers (ASME) Power Test Code 27[2] and the American Society for Testing and Materials (ASTM) D 3685-78 (Method A).[3]] Figure C-1 illustrates the Reference Method 17 sampling train. For the purposes of this discussion, the important components of the train are 1) the sampling nozzle and 2) the in-stack filter holder, which contains the filter during sampling.

Reference Method 17 is used to test particulate matter control equipment when it can be shown that results will equal those obtained by Reference Method 5. The stated criterion for the use of Reference Method 17 is that the particulate matter mass concentration associated with the subject effluent stream show no temperature dependence.[1] (Since particulate matter is defined essentially in terms of Reference Method 5, however, both the preceding applicability statements have the same meaning.)

From a technical standpoint, results of Reference 17 should strictly represent the filterable particulate matter portion of the sampled effluent stream. Nevertheless, artifact-forming mechanisms can be postulated because the particulate matter is concentrated at the filter. Accordingly, one of

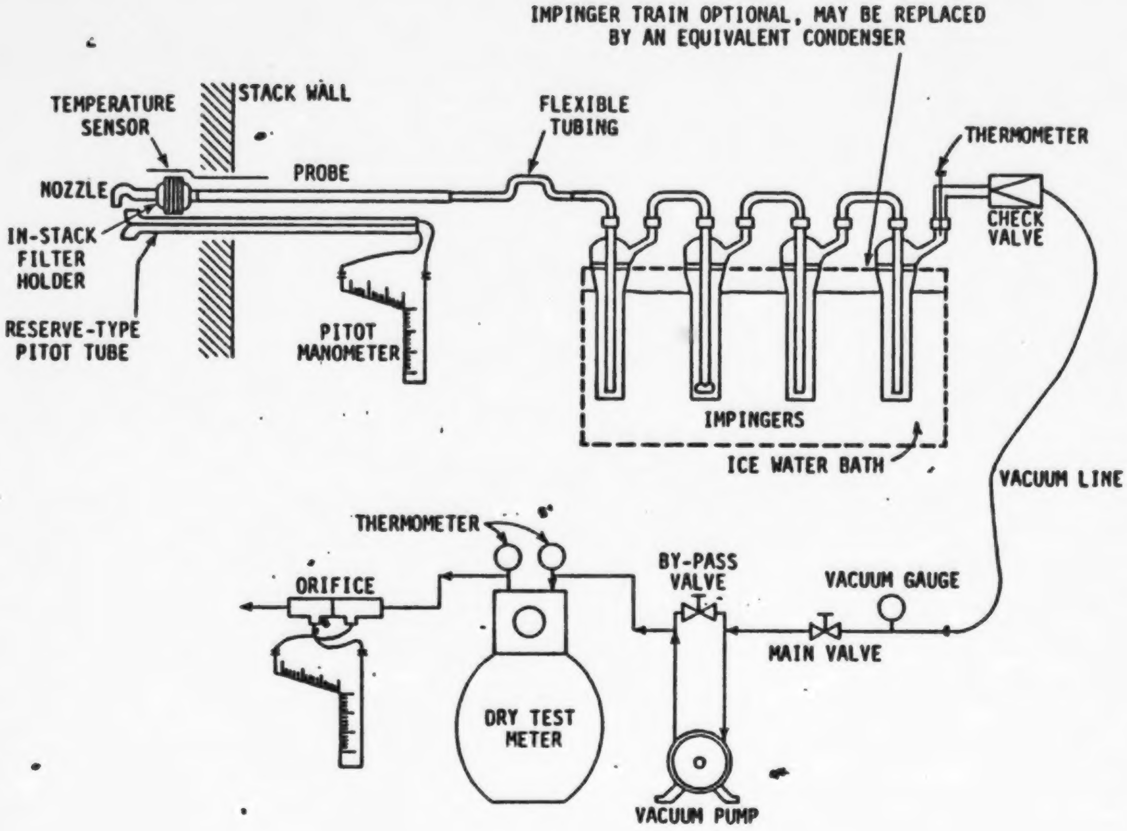

IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
TEMPERATURE SENSOR
STACK WALL
FLEXIBLE TUBING
THERMOMETER
PROBE
NOZZLE
CHECK VALVE
IN-STACK FILTER HOLDER
RESERVE-TYPE PITOT TUBE
PITOT MANOMETER
IMPINGERS
ICE WATER BATH
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY TEST METER
VACUUM PUMP

Figure C-1. Reference Method 17 sampling train.

the general principles of chemical reactivity indicates that rates increase as the concentrations of reactants increase. This argument applies to effluent streams from combustion processes. For example, effluent streams from coal-fired boilers contain alkaline fly ash and acidic gases (e.g., sulfur trioxide); when these alkaline and acidic components react, the result would be an increase in fly ash (i.e., particulate matter) mass. Because the formation of artifacts resulting from filtration-concentration reactivity has not been investigated, the impact of this postulated phenomenon on filterable particulate matter determinations is unknown. This phenomenon, however, is general; therefore, artifact formation via concentration effects are possible for all methods that entail filtration for separating particulate matter from reactive effluent sample streams. Concentration effects are also possible and have been observed on methods that entail the collection of particulate matter by impingement in water. (This subject is discussed further under EPA Reference Method 5.)

It should be recognized that the issue of "concentration artifacts" is a reflection of the inability of the in-stack method to duplicate (or simulate) the particulate matter removal processes that are common to the plume.

EPA REFERENCE METHOD 5

Reference Method 5[4] is the method used most frequently to determine mass concentrations of particulate matter within stationary source effluent streams. Method 5 is specified for assessing the performance of particulate matter control equipment installed at sources subject to New Source Performance Standards. The Reference Method 5 sampling train is illustrated in Figure C-2.

For this discussion, the important features of the sampling train are 1) the heated probe and 2) the out-of-stack filter enclosed within a heated box. These two components of the sampling train are commonly referred to together as the "front half," a term that distinguishes this section of the train from the "back half," which is the term applied to the set of impingers that follow the filter. (The back half is further discussed later in this section.) During sampling, the probe and the box that houses the filter are both heated to ensure that filtration occurs at 248 ± 25°F (120 ± 14°C).

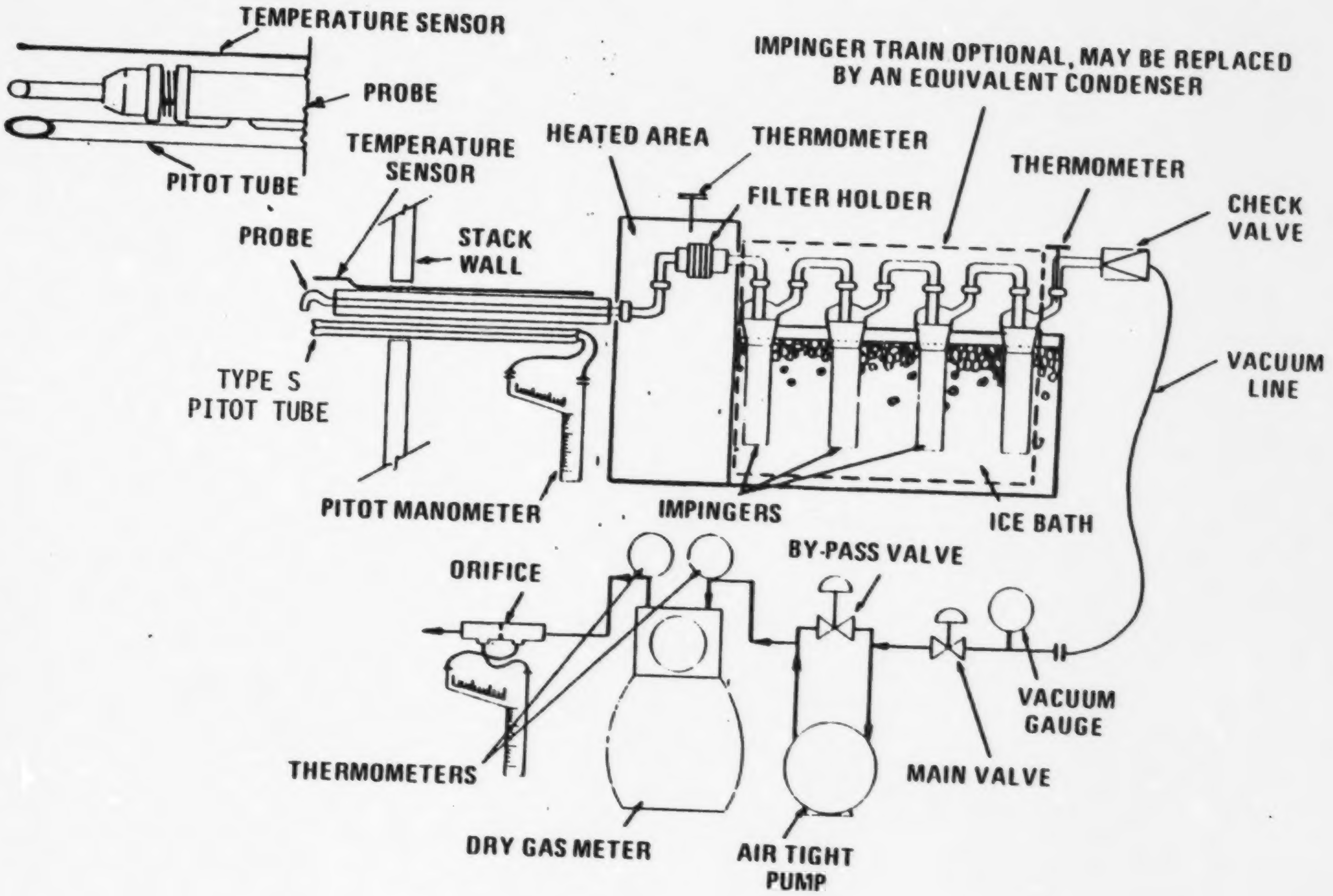

TEMPERATURE SENSOR
PROBE
PITOT TUBE
TEMPERATURE SENSOR
PROBE
STACK WALL
TYPE S PITOT TUBE
PITOT MANOMETER
HEATED AREA
THERMOMETER
FILTER HOLDER
IMPINGER TRAIN OPTIONAL, MAY BE REPLACED BY AN EQUIVALENT CONDENSER
THERMOMETER
CHECK VALVE
VACUUM LINE
IMPINGERS
ICE BATH
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
THERMOMETERS
DRY GAS METER
AIR TIGHT PUMP

Figure C-2. Reference Method 5 sampling train.

The following is the Reference Method 5 definition of particulate matter as the term applies to stationary sources subject to NSPS:[5]

> "Particulate matter" means any finely divided solid or liquid material, other than uncombined water, as measured by Method 5 of Appendix A to this part or an equivalent or alternative method.

The out-of-stack filtration technique is in accordance with a reference method approach to assessing performance[6] because all particulate matter determinations effectively fall within a consistent (i.e., reference) temperature range of collection. The specified controlled temperature is a critical parameter because the formation of condensed particulate matter is sensitive to temperature.

EPA did not intend to include sulfuric acid as part of the filterable particulate for Subparts D and Da. Accordingly, higher filtration temperatures ($\leq$ 320°F ($\leq$ 160°C)) are permitted when Reference Method 5 is applied at fossil fuel-fired steam generators having high concentrations of sulfuric acid mist within their effluent streams.[7] This variation to Method 5 is an important issue because it illustrates the limitations of particulate matter measurements as viewed from two conceptual levels. First, the characterization of particulate matter in chemical terms (e.g., sulfuric acid) is noteworthy here. Because particulate matter is invariably characterized only in physical terms, particulate matter measurement is rarely interpreted in light of filterable and condensable components; these are best distinguished on the basis of an understanding of chemical composition. This limitation is general for all the methods that are used to determine gross particulate matter.

Second, the variation noted above underscores a limitation of Reference Method 5 sampling for determining the quantity of condensed particulate matter. The measured filterable particulate matter may contain a large portion of condensed particulate matter. Thus, a significant temperature difference may exist between the effluent stream at the measurement point and the effluent stream at the point of filtration. If such a temperature difference exists and if the effluent stream contains condensable components, it is possible for these components to condense and be quantified in the front half of the Reference Method 5 sampling train. To ensure reproducibility of emission measurement results, the probe and filter temperatures are specified by the applicable regulation. Comparative results from concurrent particulate matter sampling by Reference Methods 5 and 17 sampling trains at fossil fuel-fired steam generators[8] and at portland cement plants[9] have shown that such condensed particulate matter is not only possible, but may be significant. Recent studies have been conducted on several source categories that involve the combustion of fossil fuel to determine the portion of the filterable particulate that is condensed particulate matter in the form of sulfates. The findings have not been published.

Other factors affect the interpretation of Reference Method 5 results with regard to how well they represent mass concentrations of filterable particulate matter. For example, additional particulate may form within the sampling probe if temperatures drop below 250°F (121°C). The results of sampling train performance evaluations have shown that significant cooling may occur during traversing when considerable lengths of the probe are exposed to ambient temperatures.[10] The impact of such cooling, however, has not been quantified.

PROPOSED EPA REFERENCE METHOD 5

When Reference Method 5 was proposed in 1971,[12] particulate matter was determined from the material captured in both the front half of the sampling train (probe and out-of-stack filter) and the back half of the train (impingers which contained water). The designation of the back half catch as particulate matter became a controversial issue,[13] and the promulgated sampling method entailed only front half measurements. Thus, the major difference between the proposed and promulgated Reference Method 5 is that the proposed method entails quantification of material captured in the impingers, whereas the promulgated method does not. The sampling trains, however, are identical.

Although it is not included with the federally prescribed methods for assessing source performance, the proposed Reference Method 5 sampling methodology is applied by several state air pollution control agencies; consequently, some particulate matter emission data reflect the contribution of back half particulate matter.

Since the front half of the proposed Reference Method 5 is identical to that of the promulgated method, the arguments pertaining to the impacts of condensed particulate matter and artifacts are the same.

The effluent sample that exits the filter contains essentially no particulate matter; however, when the sample leaves the heated box, it cools, and depending on the source, particulate matter may condense as a consequence of this temperature drop. Indeed, on occasion, sulfuric acid mist condensation has been observed at this position within the sampling train. The material that condenses after the filter is included with the impinger catch during sampling train cleanup operations.

The greatest potential for condensation, however, exists as the effluent sample passes through the water contained within the impingers. The water medium effectively cools the effluent sample to temperatures that correspond roughly to ambient conditions. The use of this medium for particulate matter collection is artificial, however, because the particulate matter in this process is highly concentrated on the filter and in the impinger solution where the condensate is collected, as opposed to the plume where it is highly diluted. It should be noted that similar arguments regarding the representativeness of particulate matter measured in the impingers were central to the controversy that ultimately led to the omission of the back half catch from the promulgated Reference Method 5.[14,15]

Two aspects of the impinger collection technique warrant discussion because of their potential to effect condensation in addition to those that would occur as a natural consequence of plume cooling. First, the water itself is capable of reacting with components of the effluent that condense or dissolve. This condensation has been observed in special cases when the effluent sample stream contained reactive gaseous species. The second critical aspect of the technique relates to the fact that the water concentrates the effluent sample stream. Thus, as noted earlier in the case of filtration techniques in general, chemical reaction rates increase with concentration; this concentration process is in direct opposition to the dispersion and dilution processes that characterize plume behavior.

Artifact formation also may occur up to and including the analytical phase of the back half sample. Thus, artifact-forming reactions are not limited to the sampling phase of the particulate matter determination, but may continue over significant periods of time. In short, if artifact-forming reactions are occurring, their effect will generally be magnified.

Very little information pertinent to these condensation artifacts is currently available. This state-of-the-art reflects the fact that chemical characterization is necessary before any generalizations can be made regarding the origin of the material captured in the impingers. Chemical characterizations are expensive; also, they are seldom germane to sampling operations. It should be noted that the importance of back half characterization with regard to the interpretation of particulate matter measurement results is emphasized within ASTM D3685-78 (Method B).[3]

STACK DILUTION SAMPLING SYSTEM (SDSS)

The Stack Dilution Sampling System (SDSS)[16,17] is a method for determining mass concentrations of particulate matter within stationary source effluent streams. The SDSS was developed for quantifying primary inhalable particulate (IP) matter emissions which implicitly include IP of condensed particulate origin. The SDSS is distinguished from the methods discussed earlier by its ability to characterize particle size distribution and, through simulated formation, to provide measurements of condensed particulate matter. This sampling system has not been extensively field validated.

The SDSS is illustrated in Figure C-3. The important features of the system are 1) two (in series) in-stack cyclones which separate and collect two particle size fractions and which pass particles with aerodynamic sizes less than 2.5 μm, 2) a dilution chamber which simulates particulate matter formation in the source's plume at controlled conditions by mixing the effluent sample with filtered, humidified air, and 3) a hi-vol impactor and/or filter.

As indicated by the name, the essential feature of this measurement method is the dilution chamber which is designed to simulate the production of condensed particulate matter in the plume as it cools and mixes with the atmosphere. This simultation ability is a feature that distinguishes the SDSS from the other described methods which are not intended strictly for use in quantifying the condensed particulate matter fraction of stationary source primary particulate matter emissions. Thus, the SDSS has the potential capability of characterizing the particle size distribution of the primary particulate matter.

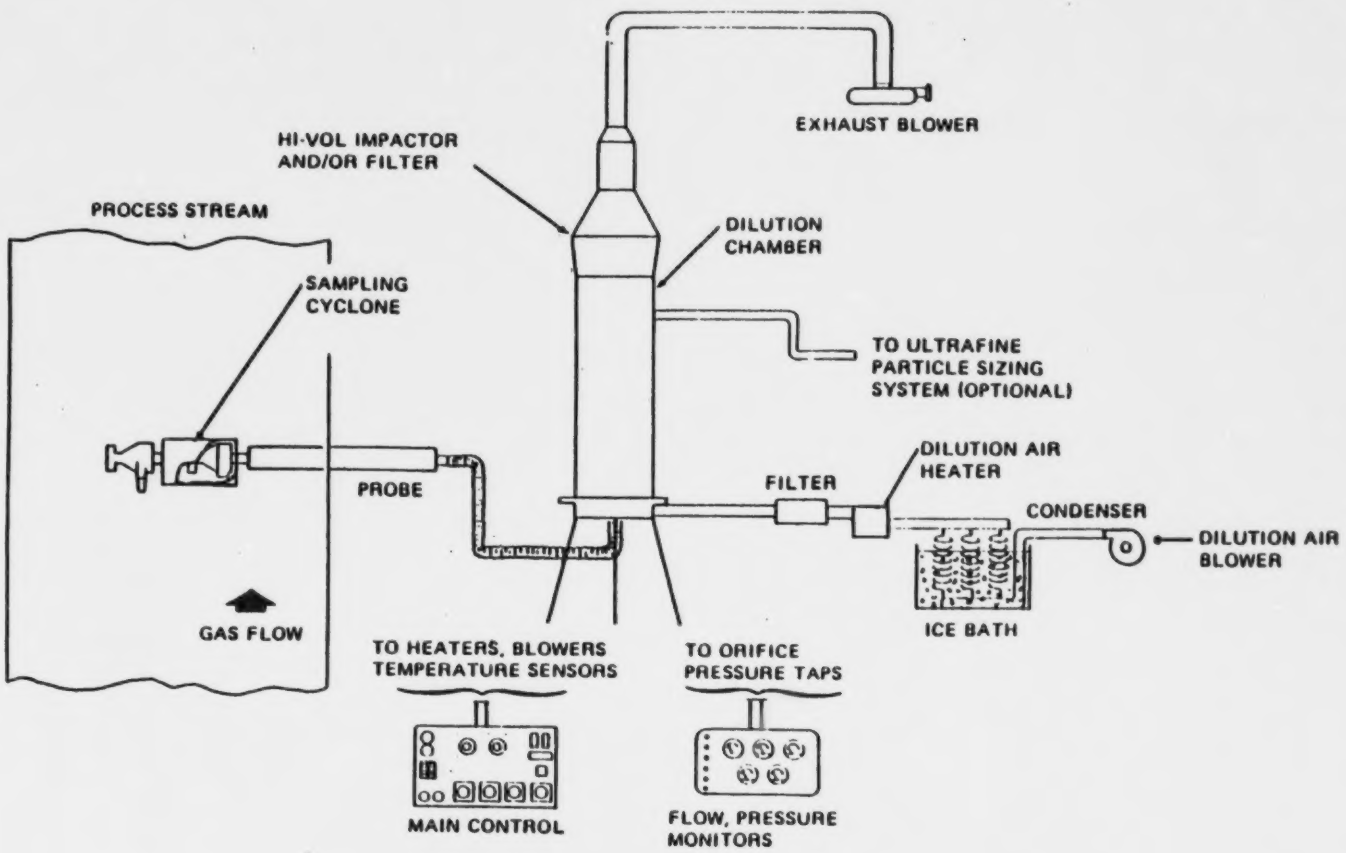

HI-VOL IMPACTOR
AND/OR FILTER
EXHAUST BLOWER
PROCESS STREAM
DILUTION
CHAMBER
SAMPLING
CYCLONE
TO ULTRAFINE
PARTICLE SIZING
SYSTEM (OPTIONAL)
DILUTION AIR
HEATER
FILTER
PROBE
CONDENSER
DILUTION AIR
BLOWER
GAS FLOW
ICE BATH
TO HEATERS, BLOWERS
TEMPERATURE SENSORS
TO ORIFICE
PRESSURE TAPS
MAIN CONTROL
FLOW, PRESSURE
MONITORS

Figure C-3. Diagram of stack dilution sampling system.

The performance of the SDSS has been evaluated at several stationary sources, including a coal-fired power plant, kraft recovery boilers, and a continuous drum-mix asphalt plant. The results of all of these tests are in substantive agreement with predictions. For example, results from particle size characterizations of the diluted effluent samples were consistent with the formation of sulfuric acid aerosol, the existence of which was predicted from independent determinations of the precursor compound, sulfur trioxide.

Although the SDSS currently appears to be the most attractive method for quantifying primary particulate matter emissions from stationary sources, the accuracy of this method has not been established. This shortcoming is not necessarily a drawback, however, because in principle the SDSS can be applied in a reference method fashion.

Tests were performed with the SDSS train at two kraft pulp mill recovery boilers, a drum-mix asphalt plant, and a coke quench operation.[16] Table C-1 presents the average condensed particulate matter expressed as the percentage of the total catch for each test, along with the average results from Method 5 tests at similar sources.

A comparison of the available data tends to confirm the fact that Method 5 collects condensed particulate matter in the filterable particulate catch. By removing some of the condensed particulate matter in the front half of the train, the back half catch is less proportioned than the measured condensed particulate portion of the SDSS.

Drum-mix asphalt plants are the only source category for which an emission factor (0.008 lb of condensed organics per ton of asphalt paving product) has been reported. The emission factor calculated for the purpose of this report (0.03 lb of condensed material per ton of asphalt paving produced) was based on EPA emission factors (AP-42)[18] and an average of Method 5 test results. The method used to calculate this emission factor was based on only two SDSS source tests; however, if a calculation is made by applying the percent condensed particulate matter reported in the SDSS tests to the Method 5 data collected, the result is an emission factor of 0.03 lb of condensed material per ton of asphalt paving produced. This emission factor is the same as the one calculated by using Method 5 back half data and AP-42.

TABLE C-1. COMPARISON OF CONDENSED PARTICULATE TEST RESULTS BY SDSS AND METHOD 5

Process	% Condensable	
	SDSS	Method 5[a]
Kraft recovery boiler (with direct contact evaporation)	33.15	No data
Kraft recovery boiler (no direct contact evaporation)	81.8	14.3
Drum-mix asphalt plant	45.45	32.1
Coke quenching	34.2	No data

[a] Results represent back half or impinger catch percentage.

REFERENCES

1. Federal Register, Vol. 43, No. 37 - Thursday, February 23, 1978.

2. American Society of Mechanical Engineers. Determining Dust Concentration in a Gas Stream. Performance Test Code 27-1957. New York, New York.

3. American Society for Testing and Materials. Standard Test Method for Particulates Independently or for Particulates and Collected Residue Simultaneously in Stack Gases. ASTMD 3685-78. 1980.

4. Federal Register, Vol. 36, No. 247, Thursday, December 23, 1971.

5. Code of Federal Regulations, Title 40, Part 60, Subpart A, Section 60.2.

6. Federal Register, Vol. 37, No. 55 - Tuesday, March 21, 1972.

7. Federal Register, Vol. 40, No. 194 - Monday, October 1975.

8. Kendall, D. R. Recommendations on a Preferred Procedure for the Determination of Particulate in Gaseous Emissions. JAPCA, 26:871, 1976.

9. Hower, J. E., Jr., R. N. Pesut, and W. M. Henry. Evaluation of Stationary Source Particulate Measurement Methods. Volume I, Portland Cement Plants. EPA-600/2-75-051a, June 1975.

10. Vollaro, R. F. An Evaluation of the Current EPA Method 5 Filtration Temperature Control Procedure, in Stack Sampling Technical Information, A Collection of Monographs and Papers. Vol. IV. EPA-450/2-78-042d, October 1978.

11. Peters, E. T., and J. W. Adams. Evaluation of Stationary Source Particulate Measurement Methods. Volume III. Gas Temperature Control During Method 5 Sampling. EPA-600/2-79-115, June 1979.

12. Federal Register, Vol. 36, p. 15704, August 17, 1971.

13. Hemeon, W. C. L., and A. W. Black. Stack Dust Sampling: In-Stack Filter or EPA Train. JAPCA, 22:516, 1972.

14. Hillenbrand, L. J., R. B. Engdahl, and R. E. Barrett. Chemical Composition of Particulate Air Pollutants From Fossil-Fuel Combustion Sources. U.S. EPA Report. March 1, 1973.

15. Kowalczyk, J., et al. Source Test Procedure for Determination of Particulate Emissions From Veneer Driers. Publication of the Control Agency Directors - Eight-Source Test Committee, Pacific Northwest International Section, Air Pollution Control Association. September 1972.

16. Williamson, A. D., J. D. McCain, W. B. Smith, and D. B. Harris. A Stack Dilution Sampling System for the Measurement of Condensible Vapors in Process Emissions. Presented at the Third Symposium on Advances in Particulate Sampling and Measurement, Daytona Beach, Florida, October 1981.

17. Heinsohn, R. J., J. W. Davis, and K. T. Knapp. Dilution Source Sampling System. Environmental Science and Technology, 14:1205, 1980.

18. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. AP-42.

APPENDIX D

CONTROL TECHNIQUES FOR CONDENSED PARTICULATES

The following are more detailed descriptions of add-on control devices that can be used to remove condensed particulate.

POSITIVE-CORONA TWO-STAGE ELECTROSTATIC PRECIPITATOR

The positive-corona two-stage electrostatic precipitator (ESP) is commonly used to collect organic aerosols in low-temperature gas streams. The gas stream is cooled to between 90° to 120°F (32° to 49°C) by evaporative cooling (direct contact), indirect heat exchangers, or dilution air. The condensed particles are charged in the first stage of the ESP by use of a wire electrode and high current. The particles are then placed in a high-potential field in the second stage and collected on metal plates. Because the aerosol is liquid and is spread over the collection surface, it forms a film of viscous organic material which is continuously drained from the plates. When the particulate matter to be collected is sticky, water spray, detergents, and periodic steam cleaning are used to form an emulsion that will drain from the surface. These collectors can effectively reduce visible emissions from 100 to <5 percent opacity. Removal efficiency may be as high as 99.5 percent. The collection is not particle size selective, and regeneration of particles does not occur from the plates. The effectiveness of control is limited only by the inlet gas temperature.

The only serious problems with these control devices are that they 1) are generally small (<30,000 acfm), 2) require precleaners to remove solid particulates, and 3) are subject to fires. Typical applications are in the textiles, rubber, vinyl, asphalt roofing, printing, grain drying, and food industries.

WET ELECTROSTATIC PRECIPITATORS

The major problem in controlling condensed particulate in dry collection devices is that the gas stream usually must be cooled below the moisture or acid dew point, which causes collection surface fouling, bag blinding, and corrosion. The wet ESP is manufactured from corrosion-resistant materials or has resistant surface coatings such as epoxy or rubber. The collection surfaces are constantly flooded with a film of water, which prevents material from coating the collection surface and fouling the collection. Also, because particles are wetted when they reach the collection surface, the possibility of particle reentrainment does not exist. These properties make the wet ESP an ideal device for collecting condensed particulate. The gas stream may be cooled to near-ambient conditions, and sticky or tacky materials may be collected. Emulsifying agents may be added to the water to reduce fouling in the waste handling systems. Typical applications include anode baking furnaces, mineral wool cupolas, sulfite and kraft recovery furnaces, chemical waste incinerators, steel sinter plants, elemental phosphorus furnaces, and chemical waste incinerators. Test data indicate outlet grain loadings of 0.005 to 0.03 gr/dscf, and removal efficiencies as high as 99.9 percent. Gas volumes range between 800 and 100,000 acfm per unit. Multiple modules may be used for higher gas volumes.

IONIZING WET SCRUBBERS

The collection efficiency of a packed-bed scrubber may be increased for the collection of condensed particulate by the addition of an ionizing section before the packed bed. Ionizing scrubbers are generally two-stage with a presaturation section. Units fabricated out of corrosion-resistant materials (FRP, Hastalloy) have been used to collect condensed particulate plumes containing ammonium bisulfite, H_2SO_4, HCl, and HF. Opacities have been reduced from 100 to 10 percent, and outlet grain loading is as low as 0.005 gr/dscf. The scrubber cannot be applied, though, to sources containing appreciable amounts of primary particulate that would foul the packed bed.

HIGH ENERGY VENTURI

Condensed particulate may be collected by a high-energy venturi (45 to 60 in. H_2O) when the condensed particulate forms ahead of the venturi throat. A major drawback to the system is that most installations do not presaturate the gas stream, and the particles condense after the venturi throat. Also, flashing of water containing dissolved solids in the gas stream may produce condensed particulate in the submicrometer range. High-energy venturi scrubbers have been used on a wide range of process operations, including coke oven pushing, steel basic oxygen furnaces, sinter plants, lime kilns, boilers, recovery boilers, elemental phosphorus furnaces, and fertilizer processes.

Removal efficiencies vary from 40 to 99 percent, depending on scrubber design and process conditions.

FABRIC FILTERS

Fabric filters have been proven to be an effective method for controlling condensed particulate. The application of the units, however, must be limited to sources that are operated above the moisture and acid dewpoints, thus preventing the gas stream from being reduced in temperature sufficiently to allow condensation of many species. Due to this limitation, the control option may be employed only on dry gas streams where the particulate is not sticky or tacky. Removal efficiencies are high (>99%) where the air-to-cloth ratio, gas stream temperature, and filter maintenance are properly controlled. Fabric filters have been applied to condensed plumes such as glass furnaces, steel sinter plants, boilers, asphalt concrete plants, ferroalloy mills, fertilizer plants, fiberboard plants, grain dryers, gray iron foundaries, lime kilns, mineral products, incinerators, portland cement plants, secondary metal (copper, aluminum, lead, zinc) operations, tire buffing, and wood product industries.

MIST ELIMINATORS

Fiber pad mist eliminators have been used successfully to remove organic aerosols from gas streams for process use and as air pollution control devices. The gas stream must be cooled to allow condensation of the aerosol. The aerosol is formed through a tightly packed fiberglass mat, which results in particle agglomeration and coating of the liquid on the fiber structure. Collected liquors are drained from the mat by gravity and transferred to waste. The collection efficiency of the system is limited by the inlet gas temperature and the filter superficial velocity. Problems with the application of this control method are similar to that discussed under positive-corona ESP's. Fouling of the fibers and fire are major concerns. Removal efficiencies of 99.9 percent are not uncommon, and opacities may be reduced from 100 to <5 percent.

INCINERATION

Condensed organic emissions may be controlled by incineration. The application of furnaces, flares, and catalytic combustion have been widely used for some time to control organic compound emissions. Incineration destroys organic emissions by oxidizing them to carbon dioxide and water vapor. Incineration is the most universally applicable control method for organics; given the proper conditions, any organic compound will oxidize. Oxidation proceeds more rapidly at higher temperatures and higher organic pollutant content. Incinerators (also called afterburners) have been used successfully for many years on a variety of sources ranging in size from <1000 acfm to >40,000 scfm.[1]

The use of existing boilers and process heaters to destroy organic emissions provides a possible means of pollution control with small capital cost and little or no fuel cost. However, this option is severely limited in its application because: 1) the heater must be operated whenever the pollution source is operated; 2) the fuel rate to the burner cannot be allowed to fall below that required for effective combustion; 3) temperature and residence time in the heater firebox must be sufficient for combustion; 4) the volume of polluted exhaust gas must be much smaller than the burner air requirement; and 5) the source of the gas must be close to the process heater.[1] Unfortuately, few boilers or heaters will meet all these conditions.

Noncatalytic add-on incinerators (sometimes called thermal or direct-flame incinerators) may be used in some applications. In this type of incinerator, a portion of the polluted gas may be passed through the burner(s) in which auxiliary fuel is fired. Gases exiting the burner(s) in excess of 2000°F (1093°C) are blended with the bypassed gases and held at temperature until reaction is complete. The equilibrium temperature of mixed gases is critical to effective combustion of organic pollutants.[1]

A temperature of 1400° to 1500°F (760° to 816°C) at a residence time of 0.3 to 0.5 seconds is sufficient to achieve 90 percent oxidation of most potentially condensable organic material.[2]

CATALYTIC INCINERATION

The use of a catalyst in an incinerator reportedly enables satisfactory oxidation rates at temperatures in the range of 500° to 600°F (260° to 315°C) at the inlet and 750° to 1000°F (399° to 538°C) at the outlet. If heat recovery is not practiced, significant energy savings are possible by use of a catalyst. The fuel savings become less as primary and secondary heat recovery are added. Because of the lower temperatures, materials of construction savings are possible for heat recovery and for incineration.[1]

Catalysts are specific in the types of reactions they promote; however, some available oxidation catalysts will work on a wide range of organic compounds. Common catalysts are platinum or other metals on either an alumina pellet or honeycomb support; metal catalysts also can be used.

The effectiveness of a catalyst depends on the accessibility of "active sites" to reacting molecules. Every catalyst will begin to lose its effectiveness as soon as it is put into service. This must be compensated for either by overdesigning the amount of catalyst in the original charge or by raising the temperature in the catalyst to maintain the required efficiency. At some time, however, activity declines to a point where the catalyst must be cleaned or replaced. Catalysts can be deactivated by normal aging, being used at excessively high temperatures, coating with particulates, or poisoning. Catalyst lifetime of greater than one year is considered acceptable.

Catalyst material can be lost from the support by erosion, attrition, or vaporization. These processes increase with temperature. For metals on alumina, if the temperature is less than 100°F (38°C), life will be 3 to 5 years if no deactivation mechanisms are present. At 1250° to 1300°F (677° to 704°C), life drops to one year. Even short-term exposure to 1400° to 1500°F (760° to 816°C) can result in near total loss of catalytic activity.[3]

CONDENSATION

Any component of a condensable mixture can be condensed if brought to equilibrium at a low enough temperature. The temperature necessary to achieve a given vapor concentration is dependent on the vapor pressures of the compounds.

Condensation will begin when a temperature is reached at which the vapor pressure of the volatile component is equal to its partial pressure. The point where condensation first occurs is called the dew point. As the vapor is cooled, condensation continues and the partial pressure stays equal to the vapor pressure. The less volatile a compound (i.e., the higher the normal boiling point), the lower will be the amount that can remain vapor at a given temperature.[1]

ABSORPTION (SCRUBBING)

Absorption, as an air pollution control process, involves dissolving a soluble gas component in a relatively nonvolatile liquid. The absorption step is only the collection step. After the gas is dissolved, it must be recovered or reacted to an innocuous form.

Common absorbents for organic vapors are water, nonvolatile organics, and aqueous solutions.[1] Absorption is increased by lower temperatures, higher gas solubility, higher gas concentrations, higher liquid-to-gas ratios, lower gas concentrations in the liquid, and greater contacting surface. Absorption has been widely used as a product recovery step in the petroleum and petrochemical industry, where concentrations are typically very high. These products are generally recovered either by heating to lower the solubility or by distillation.

If a chemical oxidizer is present in the liquid stream, organics can be oxidized in the stream. This technique has been used to convert low concentrations of odorous compounds to less odorous forms. The expense of the oxidizing chemical, however, prevents its use where concentrations greater than a few parts per million are present.[1]

The absorption-regeneration approach for organic solvents is severely limited by the low concentrations and consequent low solubilities of most organic gases in the absorbent.

Direct contact with water may be used as a cooling method for removal of high boiling compounds to avoid opacity problems in the exhaust, but in most cases, the materials do not go into solution to any appreciable extent. If water is used for condensation in this way, water treatment may be necessary before discharge.[1]

Except in a few specialized cases, absorption is not applicable to control of organic emissions except as a preliminary step.

CARBON ADSORPTION

Carbon adsorption is applicable to most organic-emitting industries but it may be of limited use in the control of a broad range of condensed organic particulates. Carbon adsorption uses a physical phenomenon to separate organic vapors from a gas stream and to concentrate these vapors to a more manageable form. The term "sorption" applies to two types of phenomena: 1) where vapor molecules are concentrated by adsorption on the surface, and 2) where vapors are concentrated by absorption of the vapor molecules into the mass of the sorbent. Adsorption is accomplished by the use of four different types of materials: 1) chemically reactive adsorbents, 2) polar adsorbents, 3) molecular sieves, and 4) nonpolar adsorbents.[1]

When adsorption is not accompanied by chemical reaction, the process is termed physical adsorption. Preferentially, polar adsorbents adsorb polar molecules (e.g., water) and nonpolar adsorbents adsorb nonpolar molecules (e.g., hydrocarbon). Molecules of any solid are attracted to each other, and the surface molecules of the adsorption medium are subject to unbalanced forces that cause vapor or liquid molecules to be attracted to the surface. Adsorption takes place through a combination of molecular attraction (Van der Waals forces) and capillary condensation of the vapors being adsorbed in the pores provided by the extended surface of the adsorbent. Although activated carbon does not enter into chemical reaction with the adsorbed vapors, it does catalyze hydrolysis and degradation reactions of certain organic solvents such as ketones.[1]

Activated carbon is the only physical adsorbent currently in widespread use for organic vapor collection. It is a nonpolar adsorbent although it has some adsorptivity for water.[1]

For concentrations greater than a few parts per million, carbon must be used many times for economic reasons. Regeneration is required to remove adsorbed vapors and reuse the carbon. Regeneration, which is the removal of adsorbed organics from the carbon, is accomplished by bringing the bed to near equilibrium by increasing the temperature. Typical regenerants are steam, hot air, and hot inert gas. The hotter the regenerant and the longer the the regeneration period, the more adsorbed solvent that will be removed (desorbed) from the carbon bed. There is an economic optimum where adequate desorption occurs at reasonable energy cost. The residual organic compound in the bed after regeneration is called the "heel," and the "working capacity" is the difference between full capacity and the heel. Regeneration is typically about 50 percent complete for each cycle under proper (or economic) operation.[1]

The reasons for limited applicability are the possible boiling points of the adsorbed organic compounds and the energy required to regenerate the carbon bed.[1] It is possible that some condensed organic material may not be desorbed because of the high energy and temperature requirements for desorption. Polymerization reactions may produce tar-like products that will condense at the operating temperatures of carbon adsorbers and not be desorbed, which causes fouling.

Another disadvantage of carbon adsorption is its adsorption of moisture. The relative humidity must be kept below 50 percent.[1] Water formed by fuel combustion must be considered in calculating the humidity level of the gas stream.

COMBINATION CONTROL SYSTEMS

A combination of control technologies, together with the introduction of cooling air, has been applied to primary nonferrous smelters for the control of the condensed particulate arsenic trioxide (As_2O_3). Because As_2O_3 has a higher vapor pressure than either oxides of selenium or vanadium, this combination of control technologies should also be effective in controlling these condensed particulates.

At a primary copper and lead smelter in Sweden, the arsenic emissions from multihearth roasters are condensed by a cooling tower before they enter the ESP's. A scrubber system is planned for the metal-producing furnaces, which is expected to reduce furnace arsenic emissions alone from 10 to 5 tons/yr. No other details regarding these systems were available.[4]

Arsenic emissions from a gold smelter in Ontario, Canada, are controlled by a "hot ESP/cold bag" system, which has been evaluated for technology transfer to other types of smelters. Because this smelter processes only 2400 kg/h of ore concentrates, adaptation to other primary nonferrous smelters would involve a large scaleup of the control equipment.[5] Figure D-1 presents a flow diagram of the smelter and the overall control system.[5]

Figure D-2 shows the roasting and gas cleaning operations at this smelter. Gases pass through two banks of process cyclones and into the hot ESP; afterwards, off-gases from the ESP are mixed with ambient air to lower the temperature and to condense the As_2O_3. Particulates, some as a vapor, pass through

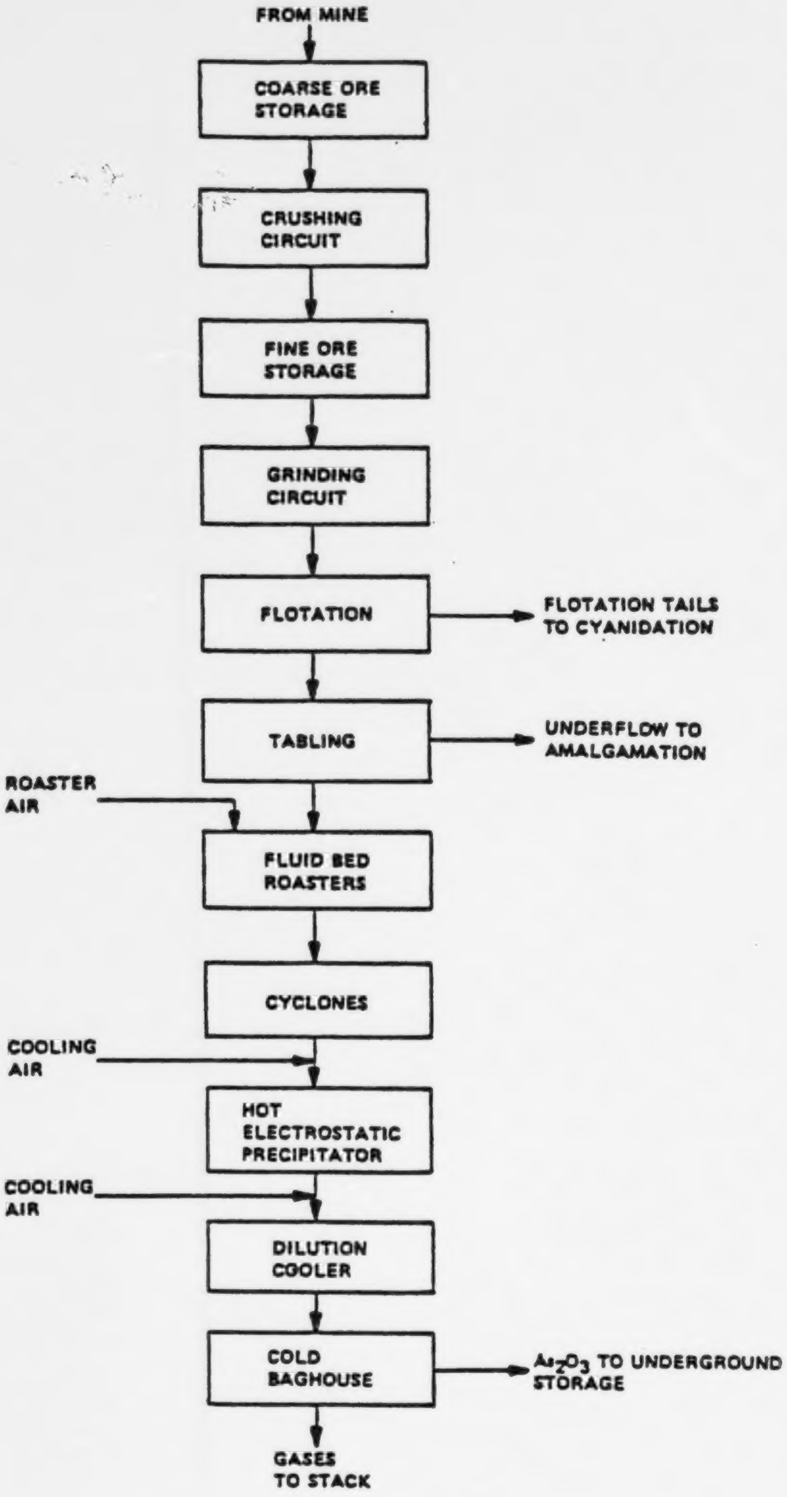

FROM MINE
COARSE ORE STORAGE
CRUSHING CIRCUIT
FINE ORE STORAGE
GRINDING CIRCUIT
FLOTATION
FLOTATION TAILS TO CYANIDATION
TABLING
UNDERFLOW TO AMALGAMATION
ROASTER AIR
FLUID BED ROASTERS
CYCLONES
COOLING AIR
HOT ELECTROSTATIC PRECIPITATOR
COOLING AIR
DILUTION COOLER
COLD BAGHOUSE
As2O3 TO UNDERGROUND STORAGE
GASES TO STACK

Figure D-1. Gold smelter flow diagram.

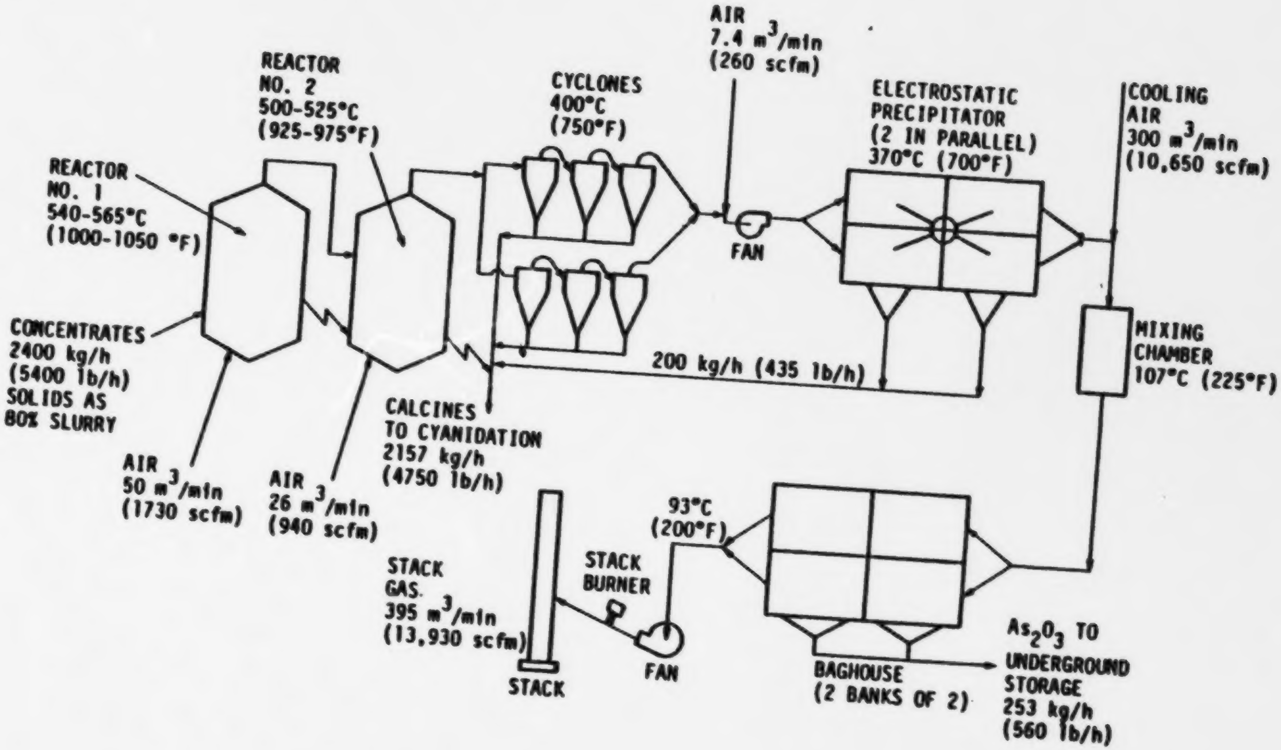

REACTOR
NO. 1
540-565°C
(1000-1050 °F)
CONCENTRATES
2400 kg/h
(5400 lb/h)
SOLIDS AS
80% SLURRY
AIR
50 m3/min
(1730 scfm)
REACTOR
NO. 2
500-525°C
(925-975°F)
AIR
26 m3/min
(940 scfm)
CALCINES
TO CYANIDATION
2157 kg/h
(4750 lb/h)
CYCLONES
400°C
(750°F)
AIR
7.4 m3/min
(260 scfm)
FAN
ELECTROSTATIC
PRECIPITATOR
(2 IN PARALLEL)
370°C (700°F)
200 kg/h (435 lb/h)
COOLING
AIR
300 m3/min
(10,650 scfm)
MIXING
CHAMBER
107°C (225°F)
93°C
(200°F)
BAGHOUSE
(2 BANKS OF 2)
As2O3 TO
UNDERGROUND
STORAGE
253 kg/h
(560 lb/h)
STACK
BURNER
FAN
STACK
GAS
395 m3/min
(13,930 scfm)
STACK

Figure D-2. Gold smelter roasting and gas-cleaning operations.

the hot ESP to the mixer-cooler and then to a four-chamber fabric filter, where they are collected. The As_2O_3 dust from the fabric filter is removed periodically and conveyed to underground storage. The reheat stack burner just prior to the stack (see Figure D-2) is not required in normal operation.[5]

Electrically heated air is circulated between the double walls of the ESP to prevent condensation of As_2O_3 on the inner walls. Two chambers are located in each of two parallel banks, but only one transformer-rectifier (T-R) set serves all four chambers.

The walls of the mixer-cooler used to condense As_2O_3 in the gas stream from the ESP are heat-traced and insulated up to the mixing chamber to prevent condensation on the duct walls. Ambient air is fed into the center of the mixer-cooler, and hot gases from the ESP are fed tangentially to create a swirling action. Ideally, As_2O_3 condenses in the gas stream of the mixing chamber at about $107^{\circ}C$. The four-chamber fabric filter is insulated and the stack is double-walled to avoid wall condensation.

Capture efficiencies for total arsenic were 15 percent for the ESP and 99.8 percent for the ESP and fabric filter. The emission rate of arsenic was 179 kg/h at the ESP inlet and 0.20 kg/h at the outlet of the fabric filter, which yielded an overall control efficiency of 99.9 percent for arsenic emissions.[5]

REFERENCES

1. U.S. Environmental Protection Agency. Control of Volatile Organic Emissions From Existing Stationary Sources - Volume I: Control Methods for Surface-Coating Operations. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. EPA-450/1-76-028, November 1976.

2. Shell Development Company. After Burner Systems Study. Emeryville, California. EPA-R2-72-062, August 1972.

3. MSA Corporation. Package Sorption Study. Evans City, Pennsylvania. EPA-R2-73-202, April 1973.

4. Lindau, L. Emissions of Arsenic in Sweden and Their Reduction. U.S. Department of Health, Education, and Welfare. Public Health Service. National Institute of Health. Environmental Health Perspectives, 19:(8) 25-29, 1977.

5. U.S. Environmental Protection Agency. Second Symposium on the Transfer and Utilization of Particulate Control Technology. Vol. III. Particulate Control Devices. Denver, Colorado. EPA-600/9-80-039c, July 1979. pp. 484-507.

APPENDIX E

TEST METHODS FOR MOBILE SOURCES INCLUDING DATA SUMMARY AND CORRECTION FACTOR

TEST METHODS FOR MOBILE SOURCES

Sampling emissions from mobile sources is difficult because the sampling equipment is stationary but the source is not. This problem is overcome by operating the source in a stationary position on a dynamometer and attaching the sampling apparatus to the exhaust pipe. Figure E-1 illustrates a sampling system approved by Federal Testing Procedures (FTP). The exhaust gas enters the dilution chamber and is mixed with ambient air. A sample is then taken by a particulate probe and a heated probe to determine the total hydrocarbon emissions. The sample taken by the particulate probe leads to two sets of primary and backup filters which are used to determine the amount of particulate-bound organics present in the gaseous stream. The cool particle test, the procedure for determining particulate-bound organics, is as follows: the emissions are collected on Teflon-coated glass fiber filters and extracted by methylene chloride extraction. The solution is then concentrated and analyzed by gas chomatography to determine the composition.

The primary and backup filters also aid in determining an acceptable level of collection efficiency. If backup filter weight gain is less than 5 percent of the combined primary and backup filter weight gain, then only the primary filter weight gain is used in the emission rate calculation. If the value is greater than 5 percent, the total weight gain of both filters must be used.[1]

Several methods of exhaust dilution are commonly used in mobile source emission testing procedures. Figure E-2 illustrates the baffle mixing system and Figure E-3 shows the turbulent-flow tunnel. The difference between these two methods is primarily the technique for diluting exhaust gas. The baffle mixing system contains a baffle arrangement to mix the exhaust with ambient air, whereas the turbulent-flow tunnel mixes the gases with turbulent flow. A small amount of particulate (6 percent) is lost when using the baffle system. Both systems, however, result in complete mixing of the gases.[1]

Mobile source sampling systems have many problems including sample validity when using standard dilution tunnel techniques and the necessary filter material for accurate pollutant collection. The latter is only a minor problem, and will be discussed only briefly. The problem of primary concern is the validity of samples.

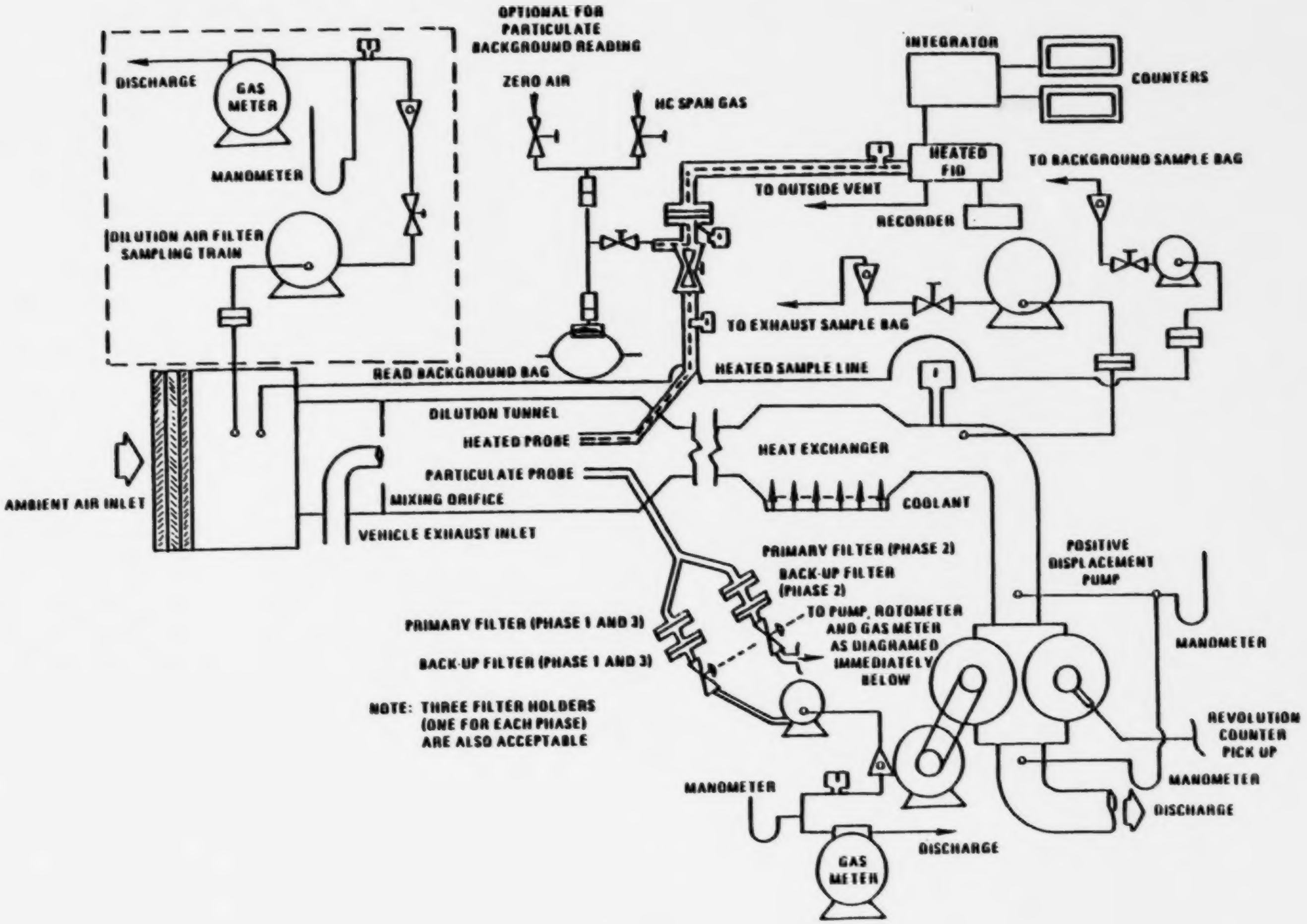

OPTIONAL FOR PARTICULATE BACKGROUND READING
DISCHARGE
GAS METER
MANOMETER
DILUTION AIR FILTER SAMPLING TRAIN
ZERO AIR
HC SPAN GAS
INTEGRATOR
COUNTERS
HEATED FID
TO BACKGROUND SAMPLE BAG
TO OUTSIDE VENT
RECORDER
TO EXHAUST SAMPLE BAG
READ BACKGROUND BAG
HEATED SAMPLE LINE
DILUTION TUNNEL
HEATED PROBE
HEAT EXCHANGER
PARTICULATE PROBE
COOLANT
AMBIENT AIR INLET
MIXING ORIFICE
VEHICLE EXHAUST INLET
PRIMARY FILTER (PHASE 2)
BACK-UP FILTER (PHASE 2)
POSITIVE DISPLACEMENT PUMP
TO PUMP, ROTOMETER AND GAS METER AS DIAGRAMED IMMEDIATELY BELOW
PRIMARY FILTER (PHASE 1 AND 3)
BACK-UP FILTER (PHASE 1 AND 3)
MANOMETER
NOTE: THREE FILTER HOLDERS (ONE FOR EACH PHASE) ARE ALSO ACCEPTABLE
REVOLUTION COUNTER PICK UP
MANOMETER
MANOMETER
DISCHARGE
DISCHARGE
GAS METER

Figure E-1. Federal emissions certification sampling system.[1]

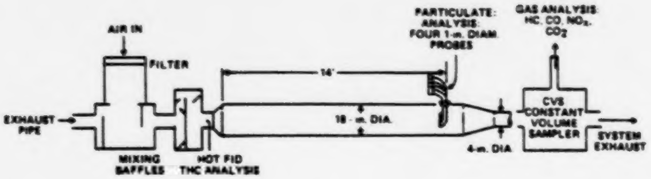

AIR IN
FILTER
EXHAUST PIPE
MIXING BAFFLES
HOT FID THC ANALYSIS
14'
18 - in. DIA.
PARTICULATE: ANALYSIS: FOUR 1-in. DIAM. PROBES
GAS ANALYSIS: HC, CO, NO$_x$, CO$_2$
CVS CONSTANT VOLUME SAMPLER
4-in. DIA.
SYSTEM EXHAUST

Figure E-2. Baffle mixing system.[2]

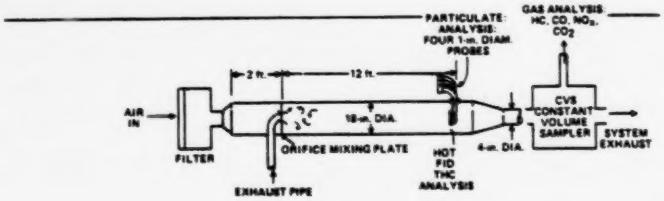

PARTICULATE: ANALYSIS: FOUR 1-in. DIAM. PROBES
GAS ANALYSIS: HC, CO, NO$_x$, CO$_2$
2 ft.
12 ft.
AIR IN
FILTER
18-in. DIA.
ORIFICE MIXING PLATE
EXHAUST PIPE
HOT FID THC ANALYSIS
4-in. DIA.
CVS CONSTANT VOLUME SAMPLER
SYSTEM EXHAUST

Figure E-3. Turbulent-flow-tunnel.[2]

The two main problems affecting the validity of samples collected from dilution tunnels are the variations in the dilution ratio and the general inability of dilution systems to correctly simulate atmospheric conditions. The use of constant-volume-sampling dilution systems, in which the total flow is constant (i.e., changes in the exhaust emission rate changes the amount of dilution air added), results in large variations in the dilution ratio and mixture temperature.

When Black and High tested the effects of the changing dilution ratio on a heavy-duty diesel engine, they found SOF increased from 31.3 percent to 32.9 with an increase of dilution ratio from 10:1 to 275:1.[2] When a similar test at a dilution ratio of 20:1 showed 29.0 percent SOF, they concluded that there was no statistical significance in increased condensed particulate from a dilution ratio of 10:1 to 275:1. MacDonald et al. demonstrated that as the temperature is increased while maintaining a constant dilution ratio, the amount of condensed material collected drops.[3] The increased filter temperature causes evaporation/desorption and prevents condensation/adsorption of the organic compounds which decreases the percentage collected. Federal testing procedures specify that the temperature at the sample probe should be at or below 125°F (52°C), but the significance of this temperature has not been demonstrated.[3]

The method for sampling particulates emitted by motor vehicles involves dilution of the total exhaust flow with filtered ambient air prior to collection. Undiluted exhaust is not sampled because the results may be biased, in that both physical and chemical properties of the emissions are affected by temperature and dilution.[1]

Dilution with ambient air permits particle-particle and particle-gas interactions similar to those that occur under actual driving conditions; however, these interactions are only approximations. The dilution of vehicle exhaust cannot be simulated in the lab.[2] Tests conducted at the University of Minnesota indicate that the dilution ratio 2.5 meters behind a vehicle moving at low speed is approximately 200:1, at 8 meters behind the vehicle, the ratio reaches 1000:1.[4] The dilution ratios most commonly used in mobile source sampling, though, are less than 50:1. The use of larger, more representative dilution ratios would require prohibitively long sampling periods to get concentrations compatible with existing sampling analytical technology.

After the exhaust is diluted with ambient air, it passes through the filter material for particle collection. Particles are collected by diffusion deposition, direct interception, gravitational deposition, electrostatic deposition, deposition by molecular forces, and inertial deposition. The importance of these individual mechanisms varies, depending on the filter type, the gas velocity, the particle shape, and the characteristics of the material being collected.

The two basic types of filters are membrane and fiber filters. In membrane filters, gas flows through pore-like passages in a thin membranous material, whereas in fiber filters, gas flows through a deep filament network of fiberous material. The primary mechanism of collection in membrane filters is direct interception. The primary mechanism for collection in fiber filters is diffusion deposition until a "clogged" state is reached (characterized by an increase in the pressure drop across the filter), at which time direct interception becomes the dominant process.[1]

Two basic types of fiber filters are generally used today: 1) glass and 2) Teflon-coated glass fiber filters. Glass filters, which have been used for many years, are currently being replaced with Teflon-coated glass fiber filters because the latter have the advantages of being less hygroscopic, more mechanically sound, and easier to handle. In addition, glass filters were found to adsorb some gaseous organic pollutants. This was demonstrated by Black and High when they tested glass and Teflon coated glass fiber filters and found that the glass filters adsorbed 25 to 32 percent of the gaseous organics collected in tests on diesel engines.[2]

DATA SUMMARY AND CORRECTION FACTOR

The filter temperature affects the amount of condensed material collected; as the temperature increases, the collection efficiency drops. MacDonald, et al. tested the effects of increasing filter temperature while maintaining a constant dilution ratio.[4] A 46 percent decrease in the percent SOF was observed as the filter temperature increased from 35^o to 100^oC. In addition, the amount of total particulate collected decreased 13 percent. Table E-1 presents the results of this experiment. Table E-2 presents a summary of emissions collected in several recent studies. This table includes the study referenced, vehicle type, fuel type, percent SOF, emissions, and the temperature at which the emission sample was collected, along with the appropriate correction factor and the corrected emissions. The two tables cannot be directly compared because they are products of different experiments on light-duty diesel engines and, as previously stated, organic emissions can vary from 10 to 60 percent.[5] At a filter temperature of 52^oC, 95 percent of the condensed material was collected. These data support the establishment of a correction factor, 1/0.95 or 1.05, to correct for increased filter temperatures.

TABLE E-1. EFFECTS OF VARYING FILTER TEMPERATURE ON EXTRACTABLE ORGANIC COLLECTION[3]

Filter temperature, °C	Extractable organics, %	Collection efficiency compared with percent collected at 35°C, %
100	20.0	54
90	24.2	65
80	27.7	75
70	30.8	83
60	33.4	90
52	35.0	95
50	35.4	96
45	36.2	98
40	36.8	99
35	37.0	100

TABLE E-2. SUMMARY OF DATA ON CONDENSED PARTICULATE EMISSIONS FROM MOBILE SOURCES

Reference I.D. No.	Vehicle type[b]	Fuel type	Soluble organics, %	Condensed particulate emissions, g/km	Collection temperature, °C	Correction factor	Corrected emissions, g/km
24[a]	LD (FTP)	Leaded	21	0.013	≤52	1.05[c]	0.014
24[a]	LD (FTP)	Unleaded	45	0.003	≤52	1.05[c]	0.003
24[a]	LD (HWFET)[d]	Leaded	9	0.015	≤52	1.05[c]	0.016
24[a]	LD (HWFET)	Unleaded	45	0.005	≤52	1.05[c]	0.005
24[a]	LD (FTP)	Diesel	26	0.08	≤52	1.05[c]	0.084
24[a]	LD (HWFET)	Diesel	23	0.05	≤52	1.05[c]	0.053
24[a]	HD	Unleaded/ leaded gasoline	2-7	0.009-0.02	≤52	1.05[c]	0.009-0.021
24[a]	HD	Diesel	10-53	0.12 -0.33	≤52	1.05[c]	0.13 - 0.35
25[a]	HD	Diesel	62	0.27	52	1.05	0.28
25[a]	HD	Leaded gasoline	5-17	0.030	52	1.05	0.032
23[a]	LD	Diesel	15	0.047	≤52	1.05[c]	0.049
23[a]	HD	Diesel	12-50	0.12-0.50	≤52	1.05[c]	0.13 -0.53
5	LD	Diesel	14-59	0.03-0.11	≤52	1.05[c]	0.032-0.12
6	HD	Diesel	11-58	---	≤52	1.05[c]	---
26[a]	HD	Diesel	13-63	0.18-0.36	52	1.05	0.19 -0.38

[a] I.D. No. refers to main text reference numbers (preceding the appendices).

[b] LD = light-duty; HD = heavy-duty.

[c] Signifies that this factor is a maximum of 1.05. The exact factor depends on the exact temperature of the filter at the time the sample was taken.

[d] Highway Federal Emissions Test.

REFERENCES

1. Black, F., and L. High. Methodology for Determining Particulate and Gaseous Diesel Hydrocarbon Emissions. SAE Technical Paper No. 790422. 1979.

2. Black, F., and L. Doberstein. Filter Media for Collecting Diesel Particulate Matter. Environmental Sciences Research Laboratory, U.S. EPA. March 1981.

3. MacDonald, J. S., et al. Experimental Measurements of the Independent Effects of Dilution Ratio and Filter Temperature on Diesel Exhaust Particulate Samples. SAE Technical Paper No. 800185. 1980.

4. Plee, L. S., and J. S. MacDonald. Some Mechanisms Affecting the Mass of Diesel Exhaust Particulate Collected Following a Dilution Process. SAE Technical Paper No. 800186. 1980.

5. Gibbs, R. E., J. D. Hyde, and S. M. Byer. Characterization of Particulate Emissions From In-Use Diesel Vehicles. SAE Technical Paper No. 801372. 1980.

6. Hare, C. T. and R. L. Bradow. Characterization of Heavy-Duty Diesel Gaseous and Particulate Emissions, and Effects of Fuel Composition. SAE Technical Paper No. 790490. 1979.